MODERN STEEL ANALYSIS

PREFACE

In writing the present book it has been the endeavour of the author to condense into a small space practical methods for the exact estimation of all those constituents of steel which are of fairly common occurrence. It is hoped that the book will be found useful by steel analysts who do not possess either the time or the facilities for personally sifting the mass of literature which is annually published on the subject, and that it will also meet the requirements of third and fourth year students who, after a general training in chemistry, are desirous of obtaining some practical experience in analysis which is commercially important. No attempt has been made to give a comprehensive description of all the processes used in the analysis of steel, but the methods detailed have been selected for their practical utility. A section on general procedure has been included primarily to meet the needs of students without experience in chemical practice, but it is hoped that some of the hints contained therein may also be of service to other chemists.

Methods for the estimation of tantalum, columbium, tin, boron, and a few other unusual constituents of

steel have not been included in the present volume, but should this little work prove useful to chemists it is hoped to include them in a subsequent edition.

The author desires to express his indebtedness to Messrs. C. H. and N. D. Ridsdale, of Middlesbrough, for permission to publish details of their well-known mechanicalized methods.

J. A. P.

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GENERAL PROCEDURE

The following remarks are intended primarily to guide students who have pursued a general course of training but are without practical experience of procedure in a routine laboratory. Chemists daily engaged in analysis may consider many of the statements obvious or unnecessary, but it is the author's experience that students who have attained a sound theoretical knowledge are frequently lacking in the ability to perform operations in the simplest way necessary to ensure accuracy. Analytical chemistry as taught in many colleges is, to a large extent, far too academic in its quality: precautions are insisted upon, but no account is taken of their relative value. For example, before weighing an ignited precipitate of barium sulphate the addition of a drop of nitric acid followed by a drop of sulphuric acid—to convert any sulphide formed by reduction by the filter ash back into sulphate—and re-ignition is always insisted on, but the complete insolubility of barium sulphate, however precipitated and however washed, is a matter of faith. With proper ignition the error introduced by neglect of the former precaution can hardly exceed 5 per cent. of the weight of the precipitate in the most extreme cases, whereas if the precipitate be not obtained by adding the barium chloride solution slowly to the boiling sulphate solution

only 60 to 70 per cent. of the barium sulphate may be precipitated from dilute solutions in twelve hours, and if the precipitate is washed with dilute hydrochloric acid the greater part will be dissolved from off the filter again. Again, rapidity is hardly considered, nor is there any attempt to avoid the performance of unnecessarily laborious operations. For instance, a sample is weighed out by difference weighings from a weighing bottle, which establishes the weight taken accurately to about 1 in 50,000, while duplicate determinations will not agree to the third significant figure.

Weighing. Analysts are chiefly concerned with the weighing of the amount of sample taken, the final ignited precipitate, and absorption tubes.

Weighing out Sample. It is usually found desirable in practice to adjust the weight of the sample to an even number of grams, or to a convenient factor weight; as this simplifies calculations, reduces the number of notes to be made, and minimizes the liability to errors in weighing. This is most readily managed by using a small scoop, hammered or stamped out of aluminium or other sheet metal, exactly counterpoised by a suitably adjusted lump of metal placed in the pan carrying the weights. After weighing, the sample is tipped out of the scoop into the beaker or flask, and if necessary the scoop is brushed out with a fine camel-hair brush, but usually a smart tap will remove everything. In most analyses it is unnecessary to weigh the amount taken more accurately than to a milligram, although the moral effect of the fourth place is sometimes stimulating.

Precipitates. A good many precipitates, such as silica, barium sulphate, aluminium oxide, are most con-

veniently weighed by brushing out of the crucible into the balance scoop, taking precautions against loss by performing the operation over a sheet of smooth paper. In the case of powdery, non-hygroscopic precipitates this procedure is to be recommended not only on the grounds of speed and convenience, but also for its accuracy, as the chemist is thereby freed from any doubt as to the fluctuation in weight of the crucible and is certain that the weight obtained is that of the precipitate. Not all precipitates, however, can be brushed out in this manner, and in these cases the usual weighing in tared crucibles is necessary. Very hygroscopic precipitates, which are rare, may be weighed, if the greatest accuracy is desired, in crucibles enclosed in stoppered weighing bottles; but usually it is sufficient first to adjust the weights roughly, and then to place the crucible in the pan and complete the weighing as quickly as possible.

Absorption Tubes. The weighing of absorption tubes calls for no special mention. They should expose as small a surface as possible and should be polished with a soft leather before weighing. After polishing, for the greatest accuracy they should be left in the balance case for ten minutes and then weighed; neglect of this precaution may lead to an error of as much as two milligrams. Geissler potash bulbs and other fragile and intricate apparatus are quite unsuitable for practical use.

Precipitation. To obtain precipitates in such a condition that they filter readily, that is to say in moderately large and compact particles, is one of the operations in which the value of practical extended experience is inestimable. The conditions governing the formation

of proper precipitates follow no general rule, but vary from case to case. Lead molybdate and cobalt ammonium phosphate are practically unfilterable unless the liquid in which they are precipitated is well boiled. In the basic acetate precipitation of iron the liquid must be raised to boiling-point, but if boiled the precipitate becomes slimy. Cuprous thiocyanate is most satisfactory if precipitated from cold solutions after vigorous stirring, while magnesium ammonium phosphate must be precipitated from thoroughly cold solutions which are well stirred or shaken. In some cases large excesses of precipitant are desirable, in others the smallest possible excess. No general rule can be formulated and knowledge of conditions necessary is only to be gained by experience; for although it may be possible in each case to define exactly the precautions to be taken it is undesirable to burden a description with small details which are commonplaces to the man of experience.

Filtration. This operation, which by faulty manipulation may easily occupy more time than all the other operations of analysis together, when performed with skill is one of the most rapid. A volume of 300 c.c. should pass through in five minutes or less, and the rate of flow should be but little retarded when the precipitate has been transferred to the filter. Generally speaking, warm solutions filter better than cold, and acid solutions better than alkaline, but the most important point is the proper arrangement of the filtering medium. When using filter papers, funnels with deep ribs or flutings on their inside conical surface are much to be preferred to plain funnels. Plain funnels, even with a well-fitting

filter paper, in addition to filtering rather slowly sometimes allow fine-grained precipitates which go through the paper to be retained between the glass and the surface of the paper, with the result that when the filter paper is removed for ignition some of the precipitate sticks to the glass and is then rather difficult to transfer to the crucible ; or it may even be overlooked and lost.

Pulp Filtration. Filters of almost any degree of openness or fineness may be obtained by the use of filter-paper pulp, and for a given efficiency of separation filtration through pulp is quicker than through folded papers. A pulp filter is prepared in the following manner: A number of filter papers are torn (not cut) into small pieces about half an inch square or less and placed in a large flask about half filled with water, preferably hot. The flask is then stoppered and the contents thoroughly shaken until the filter paper is completely broken up into shreds. On the score of cheapness filter-paper clippings are to be recommended and serve equally well. The filter pad is now prepared by placing a perforated porcelain filter disc in the neck of a plain funnel (*see* Fig. 1), whose stem has been cut off square but not unduly shortened. Water is poured in to cover the disc, and pulp suspension added in sufficient amount, keeping the stem closed meanwhile with the finger. The filter plate is adjusted in the neck of the funnel with a glass rod and the finger removed, when the pulp sinks down and forms a pad. This is now consolidated by judicious pressure with a flat-ended glass rod, more or less pressure being used according

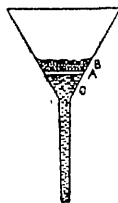



FIG. 1.

to the fineness of the precipitate to be separated. The edges of the pad are conveniently tucked in by swirling a fairly rapid stream of water from a wash bottle circumferentially over it. With such a pad even a sulphur suspension may be filtered out; while the rapidity of filtration is very satisfactory, and the washing of the precipitate greatly simplified because all the washing liquid passes through the precipitate and there are no filter-paper edges to be carefully washed. A filter pump may be used in conjunction with these pads without fear of sucking through, but attempted acceleration with a pump in most cases produces only a temporary acceleration, as with other filters, the last state being worse than the first.

Filtration through Asbestos. Many liquids which cannot be filtered through filter paper, such as permanganate and caustic solutions, may be filtered through ignited asbestos. Ordinary asbestos is ignited in a muffle and made up into a suspension with water in the same way as pulp, and a filter prepared in the way just mentioned. Special filtering asbestos can be obtained, but is much more expensive than the ordinary variety and little better. It is not advisable to use asbestos in filtration of acid liquids where contamination with metallic salts, particularly those of iron, aluminium, and magnesium, is prejudicial, as although an improvement may be made by extracting with strong hot hydrochloric acid it is practically impossible to extract everything soluble in acids.

Cotton-wool Filtration. Cotton-wool may be made use of very advantageously for certain filtrations, as it is practically ashless and withstands the action of concentrated hydrochloric acid, 1·2 nitric acid, and fairly

strong sulphuric acid very well. A cotton-wool filter is very conveniently made by pushing a pad of cotton-wool about $\frac{3}{4}$ in. long into a long tube of $\frac{1}{2}$ in. bore supported in a burette stand. This method of filtration is particularly useful in the estimation of graphite in pig-iron, as after filtration and washing are complete the pad is pushed backwards out of the tube, thereby efficiently cleaning the walls, and may be burnt off at the mouth of the muffle; the residual graphite being then weighed.

Evaporation and Baking. These operations are performed on a hot plate, which may be conveniently constructed of a sheet of steel $\frac{1}{4}$ in. thick, measuring about 2 ft. by 18 in. The plate may be supported on iron legs or on bricks, and should have burners disposed beneath it so that a range of temperature is obtained from the highest temperatures directly over the burner, which should impinge on the lower surface, to the comparatively cool corners most distant from the flame. A large spreading flame particularly suitable for heating hot plates may be obtained by using an ordinary bunsen burner whose jet has been replaced by a hole $\frac{1}{8}$ in. in diameter. Evaporations can be speedily carried out on a hot plate as the beaker can be placed on a part only just cool enough to avoid spitting. When evaporated to complete dryness, Jena beakers may be placed on the hottest part of the plate and thoroughly baked without the least danger of cracking the glass if not too suddenly cooled when removed. It is sometimes convenient to cover part of the plate with a sheet of asbestos on which beakers requiring a long digestion at a moderate temperature may be placed.

Absolute Value of Results. Where there is any doubt whether a figure obtained as a result of an analysis actually represents the true percentage of the constituent in the sample, the most satisfactory confirmation of its accuracy is obtained by going through the same series of operations using a similar solution of known composition. This is nearly always possible, and many procedures giving rise to results which would be erroneous if taken at their face value—especially in volumetric estimations—may be made to yield satisfactory figures by taking into account the behaviour of the standard or the blank determination. The standard solution should always be of as nearly as possible identical composition, not only as to the constituent under consideration and iron, but also as to the other components of the solution, dilution, acidity, &c. Often the most satisfactory way is to add a definite further amount of the doubtful constituent to the sample, carry through the analysis as before, and see whether the increased percentage found corresponds to the amount added, though this is not satisfactory in all cases. By this means a greater feeling of certainty as to the meaning of the result is obtained, and the personal equation, a very important factor in the past, can be eliminated.

Arrangement of Work. This is perhaps the most important thing to be learnt by an analyst when once he has mastered the elements of the science. The dovetailing of operations so that the worker's time can be fully used to the best advantage needs experience and forethought. A little time is well spent at the beginning of each day in taking stock of the things to be done and

arranging in what order to do them. There is then no fear either of time being wasted or of overcrowding any part of the day with too many operations, conditions which almost invariably lead to imperfect work and want of accuracy. It is perhaps hardly necessary to indicate that long evaporations should be started as soon as possible, and that while they are proceeding the shorter estimations may be carried out. Filtration should be arranged to fall in batches, so that the operator's time may be fully occupied; for it takes but little longer to filter six solutions than one if done together, though separately they would occupy six times as long. Economy of time and gas is ensured by arranging that the precipitates to be ignited are all burnt off at the same time; and it takes less time to make twenty weighings one after the other than it does to make twenty weighings separately.

Sampling. In taking samples from specimens of steel the object usually in view is to obtain a representative portion of the material in a shape suitable for analysis; but sometimes when want of homogeneity, or segregation, is suspected, sampling is performed with the intention of revealing this variation in composition. Since solidification begins from the outer surface of a casting and the impurities in the steel are both lighter and more fluid than the pure metal, it follows that the higher parts of the thickest portions of the casting will tend to contain a higher proportion of these impurities, and this fact should be borne in mind when looking for local variations.

When a representative sample only is needed material from near the surface should be avoided, particularly

if much re-heating has been performed on the specimen, as a considerable amount of carbon may have been lost under these conditions.

The method of taking the sample calls for a little notice. The usual practice is to drill the sample, using as large a drill as the sample will take and the power available permits, since a drill is the most economical tool for reducing a portion of the specimen to a handy size for manipulation in view of its requiring least power for removing a given weight of metal. Turning is also a permissible method, but filing and milling are not satisfactory—filing because the file teeth are worn away and contaminate the sample, and milling because of the great difficulty in cleaning the cutter and the trouble and expense which would be necessitated by the frequent grinding and resetting. Whichever method is employed the tool used should be sharp and used without lubricant, as it is essential to avoid studiously any contamination with carbonaceous material.

The following list contains brief instructions for suitably drilling commonly occurring shapes.

Bars. Drill transversely from side to side, neglecting drillings from surface.

Plates. Drill through in several places.

Ingots. Drill well in. Always avoid outside layers and top of ingot.

Rails. Drill parallel with the length in several places. Carbon may vary from point to point, and the samples should be kept separate and examined for carbon segregation. The other determinations should be carried out in the sample from the thickest part.

Carriage Springs. Chop off and drill ends transversely.

Sample Ingots. Drill from face to face.

Castings. These are so varied in shape that no general instructions can be given except to avoid the outside and top parts.

Useful Apparatus. There are a good many simple pieces of apparatus easily made by any good carpenter

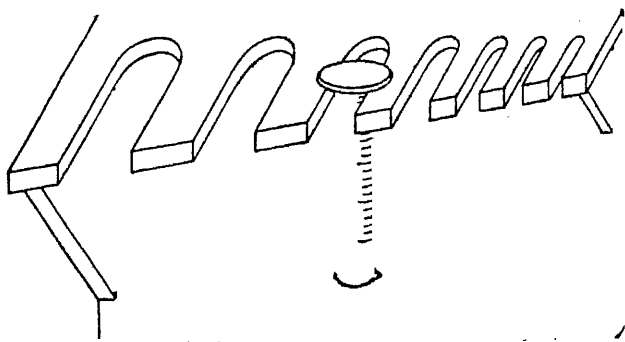



Fig. 2.

which greatly add to the convenience of working and minimize loss of time. A good draining board, a measure rack, a beaker rack, and a filtering stand are really invaluable, and the forms shown in the illustrations have been found quite satisfactory.

Draining Board. This piece of apparatus is too well known to need much description. It should consist of a sloping board with vertical pegs to support the apparatus while drying, and should be of fair size and be conveniently disposed to drain into the sink.

Measure Rack. A suitable rack may be made by

cutting a number of bays with straight sides, and of widths adapted to the measures, in a shelf. The measures are suspended in the bays by means of the flanges at the bottom and hang mouth downwards, so that they drain dry and dust does not settle in them. If a special small shelf is made for them, it should either be of stout wood or of two-ply material so as to avoid warping. A drip board may be placed below.

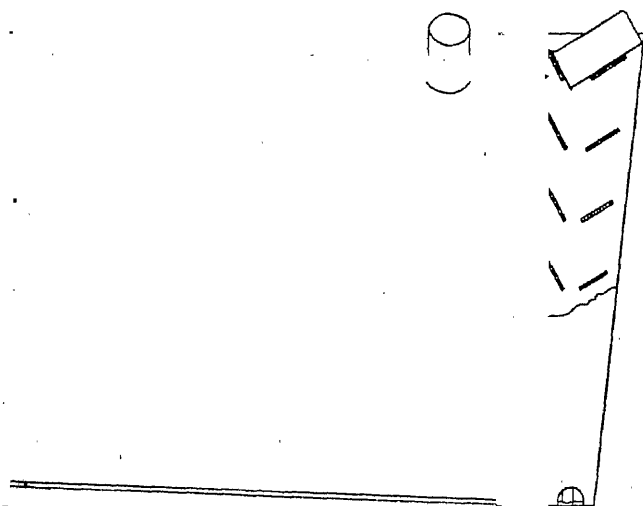



Fig. 3.

Beaker Rack. This consists of a number of slats of wood arranged to form V-shaped troughs open at the bottom, and with one side wider than the other. The wider side of the trough is arranged at an angle of about 30° with the horizontal, the shorter side being at right angles with the other. The beakers rest in the troughs

with their sides on the wider side of the trough and the rim against the other side. In this way they drain dry and dust does not collect in them. A hundred beakers can easily be kept on a wall-space measuring 4 ft. by 4 ft., and any one is instantly available for use.

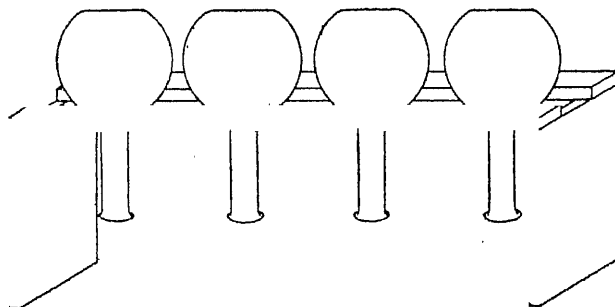



FIG. 4.

Rack for Flasks. Flasks are conveniently stored in a rack consisting of two battens or rods of wood arranged parallel to one another at such a distance apart that the neck of the flask passes between them and the flask hangs supported by its sides.

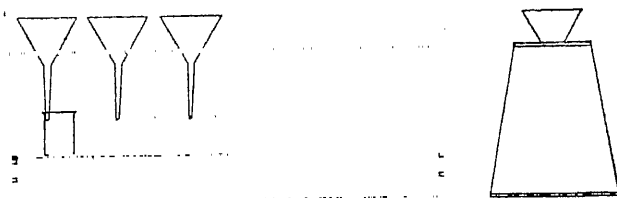



FIG. 5.

Filtering Stand. A stand to take six funnels side by side, as shown in the sketch, is very handy. It should

have a movable shelf below the funnel stems so that filtration into beakers of different depths can be carried out.

Burette Stand. Burettes are very conveniently supported in the apparatus shown, which consists of two

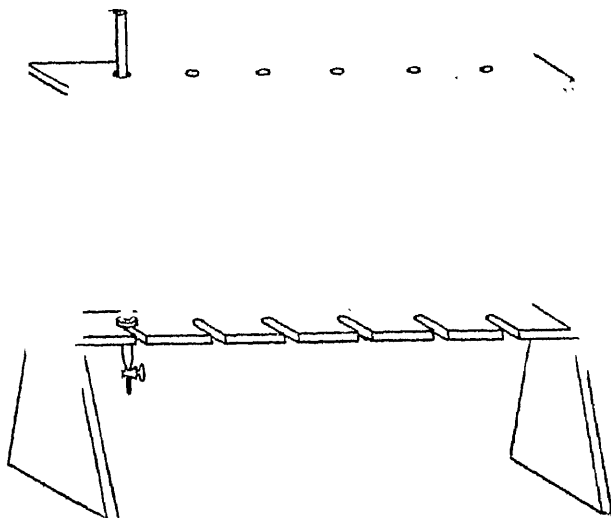



FIG. 6.

narrow shelves, the lower about 10 in. and the other 2 ft. above the bench level. The lower shelf has notches a little wider than the burettes cut in it, the upper, holes through which the tops of the burettes pass. The burettes are prevented from dropping down by a stout piece of rubber sheet slipped over them as shown: a cork will serve equally well.

ALUMINIUM

ALUMINIUM is occasionally present in steels derived from the ore from which the pig-iron was smelted, but its presence is more frequently due to the addition of aluminium in the ladle. It is chiefly important in view of its action in producing quiet casts, which effect is supposed to be due to its rapid reduction of the oxides present without elimination of gas.

In the estimation of aluminium in steel advantage is usually taken of the insolubility of aluminium phosphate in neutral solutions, ferrous phosphate being soluble. The estimation of very small amounts of aluminium with accuracy is attended with some difficulty, but fortunately the importance of traces of this element is generally considered to be small.

Estimation. Dissolve 10 or 20 grm. of the sample in 100 or 200 c.c. of hydrochloric acid (1 : 1). Boil the solution, dilute to 300 c.c. and pass H_2S until the precipitate, if any, flocks together, and filter off any precipitated copper sulphide, carbon, and silica. Boil thoroughly for ten minutes and add 25 c.c. of sodium phosphate solution (10 per cent.), followed by ammonia until a precipitate just forms and is not re-dissolved. Clear the solution by adding 2 c.c. of hydrochloric acid, add a considerable amount of acetic acid, dilute to about 400 c.c., and boil. When the solution has boiled remove it from the plate and add about a tablespoonful of

sodium thiosulphate. Boil again thoroughly for about ten minutes, allow the precipitate to settle, and filter. Wash the precipitate thoroughly with hot water and ignite. If white it may be weighed at once as $AlPO_4$; if not white it may be redissolved in a little strong hydrochloric acid, the iron precipitated by boiling with a fair excess of caustic soda, and the aluminium re-precipitated in the filtrate exactly as before after adding 10 c.c. of sodium phosphate. Al in $AlPO_4 = 22{\cdot}10\ \%$.

Chromium. Chromium if present will follow the aluminium through all the steps of the preceding estimation. It may be separated by fusing the precipitate in a platinum dish with sodium carbonate containing a very little sodium peroxide. On dissolving the melt in hot water, acidifying with sulphuric acid, adding a little more sodium phosphate, and then making alkaline with ammonia, aluminium phosphate is precipitated while chromium remains dissolved as ammonium chromate.

Tungsten. May remain undissolved to a large extent. Any passing into solution is removed by the passage of sulphuretted hydrogen.

Molybdenum. Is removed by the sulphuretted hydrogen.

Vanadium. If vanadium be present in the precipitate the procedure given above under chromium may be applied, and a fairly large excess of phosphate and ammonia added.

Titanium. This element may be present even if the precipitate is white. The precipitate should be fused with potassium bisulphate, the melt dissolved in dilute sulphuric acid, and the titanium estimated colorimetrically. The corresponding weight of titanic oxide, TiO_2, should be deducted.

ARSENIC

ARSENIC occurs in nearly all varieties of steel, and is considered to have a similar effect to phosphorus on the metal, but its influence is less marked. The following method for its estimation is probably the simplest and is not interfered with by any element commonly occurring in steel.

Estimation. Weigh 5 grm. of the sample into a 500 c.c. distilling flask fitted with a rubber stopper carrying a thermometer graduated to 120° C. Attach to the side a Will and Varrentrap absorption tube filled with bromine water and about 2 c.c. of bromine in addition. Quickly add to the flask 60 c.c. of hot hydrochloric acid (1 : 1), replace the thermometer, and heat gently until the steel is all dissolved and most of the bromine in the absorption tube has disappeared. Remove the flame and cool somewhat. Add the contents of the absorption tube to the flask and also 100 c.c. of calcium chloride solution (*see* Appendix). Attach to the side tube a small condenser and distil until the temperature reaches 115°, collecting the distillate in a conical flask. Remove the flame. The arsenic, which has been evolved as arsenious chloride and is present in the receiver as arsenious acid, is now estimated by means of iodine. Add to the receiver an equal volume of water and a little starch solution (*see*

Appendix I), and run in from a burette standard centinormal iodine solution until a blue coloration is obtained. The percentage of arsenic is calculated from the relation 1 c.c. $\frac{N}{100}$ iodine = ·000375 grm. As.

A little arsenic is occasionally present in the reagents, and in consequence a blank estimation should be made, using double the volume of reagents and the same amount of steel.

The iodine solution should be standardized against pure arsenious oxide by dissolving about 0·1 grm. in a little sodium carbonate solution, acidifying with hydrochloric acid, and titrating.

CARBON

The proportion of carbon in steel has such a far-reaching influence on the properties of the metal that it is natural for its estimation to have attracted more notice than that of any other element. New methods still continue to be suggested and applied, and some of these will be considered later. The methods at present most widely adopted are; (1) the colour comparison method; (2) the direct combustion method; (3) the wet combustion method.

Of these three methods the first is the simplest and least accurate, while the second and third are the methods relied on for specification purposes. For all ordinary steels the estimation of carbon by direct combustion in a current of oxygen is the most accurate method known, but high nickel steels are only burnt with considerable difficulty unless the drillings or turnings are very thin and a temperature of at least 1000° C. is employed. There are fewer opportunities for errors to creep into this method than in the case of the wet combustion method, and if a blank is determined before and after a series of estimations and the contents of the boat after an estimation are examined for metallic residue, which is readily done by crushing in a mortar, it is quite permissible to rely firmly on the result. In the wet combustion method, by which is

meant the method depending on the combustion in air or oxygen of the carbonaceous residue separated from the steel by solutions of double copper salts, carbon present in the steel as carbon monoxide and carbon dioxide is completely lost, and a further loss may occur through the formation of hydrocarbons through the action of the solutions on the steel. Goutal (*Comptes Rendus*, CXLVIII, 1909, p. 988) has found that in certain cases the total loss from these causes may amount to 0·0435 per cent. Copper potassium chloride is to be preferred to copper ammonium chloride for the separation, as the latter may introduce a positive error through the presence of pyridine hydrochloride, which is sometimes present. Statements that dissolved cellulose is also occasionally present have been made. In common practice the solution is made up from copper sulphate and ammonium chloride. The advantages of the method are simpler apparatus and ability to use air instead of oxygen. By suitable arrangement a large number of samples may be dealt with in this way almost as quickly as by the direct process. The process depending on solution of the steel in chromic and sulphuric acid solution containing copper, thus oxidizing the carbon to carbon dioxide, which is suitably purified, absorbed, and weighed, can be made to give accurate results, but requires more manipulative skill and takes considerably more time and attention. The glass apparatus employed in the estimation is usually both expensive and fragile, and the author prefers to use this method only for check estimations in the case of steels which are burnt with difficulty, *e.g.* high nickel and nickel chromium steels.

The well-known colour comparison method depends on the fact that when steel is dissolved in diluted nitric acid part of the carbon goes into solution, forming an orange-brown liquid. By comparing the intensity of the colour with that produced by a steel of known carbon content an estimate of the amount of carbon present can be made. This method is not to be depended on for a high degree of accuracy for several reasons. In the first place the colour developed by a given steel is dependent on its state of annealing—indeed the colour carbon method has been used to check the annealing of samples—while small differences in the composition of the standard and sample can produce a considerable difference in tint. Copper is present in varying amounts in most steels, but it would be exceptional for its influence in this estimation to be allowed for. Very large errors also may be introduced even when annealing is perfect, and the samples are similar, if the percentage of carbon in the two is not approximately the same. It by no means follows that a steel containing 0·8 carbon will yield a solution of twice the intensity produced by a 0·4 carbon steel. Nevertheless the simplicity of the operations and the ease with which a number of determinations can be made give the process considerable value where its limitations are well understood.

Stead's modification of the test, which consists in precipitating the iron and other metals with caustic soda and comparing the more intensely coloured filtrates, eliminates a good many of these disadvantages and is more accurate, though slightly more troublesome.

Colorimetric Estimation. The estimation is carried out as follows: Exactly 0·1 grm. of the sample and

0·1 grm. of a standard steel containing about the expected percentage of carbon are weighed into test-tubes. To each tube is added 2 c.c. of nitric acid (1·2) and the test-tubes are placed in a bath of boiling water —a beaker serves very well—for twenty minutes. The tubes are then removed and cooled together in another beaker of cold water. For the purpose of comparing the intensity of the colour, special tubes of similar shape and capacity are used. The standard solution is made up to 100, 200, or more times as many c.c. as it contains per cent. of carbon and transferred to one of the comparison tubes. Thus a steel containing 0·15 per cent. of carbon would be made up to 15 or 30 c.c. The sample is then washed into another comparison tube and diluted until its colour is equal to that of the standard. The tubes are most readily matched by holding them side by side in an inclined position on a white tile and looking through them. When the colours are nearly the same the left hand tube should be changed over to the right hand and back again to eliminate chance differences in lighting. The volume of the sample is then measured and the number of cubic centimetres, divided by 100, or 200, gives the percentage of carbon.

Estimation by Direct Combustion. This is carried out in the apparatus shown in Fig. 7. Oxygen from a cylinder is passed through A, which must be provided with a clip or tap, into the gasholder, B, whence it passes through the purifying tubes, C and D, containing strong sulphuric acid and soda lime respectively. Joints between different pieces of the apparatus are made with pressure tubing as this lasts very much longer

than thin-walled tubing without cracking or leaking. The combustion tube, I, which is of porcelain or silica about 1 in. in internal diameter, is connected to D by a few inches of rubber tube, E, through the tap, F, and is closed at either end by well-fitting single-holed rubber stoppers. The tube is laid in a furnace capable of attaining an orange-red heat which may be heated by gas or by electrical resistance. An electric resistance furnace is to be preferred to a gas-fired furnace largely because of the easy attainment of temperatures not readily reached in a gas furnace and also in view of its cleanness. Gas furnaces also have the disadvantage that they make the laboratory very hot, besides introducing a large quantity of carbon dioxide into the atmosphere, which is most undesirable. Silica tubes have been used to replace the porcelain, but their much higher price is not compensated by a greatly increased life. The porcelain tube is packed from the middle to near the exit end with coarse copper oxide (from wire) between plugs of ignited asbestos. If a silica tube is used it must be packed with platinized quartz. To guard the

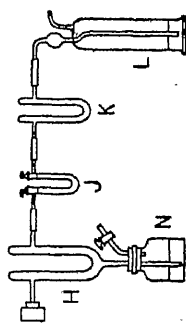
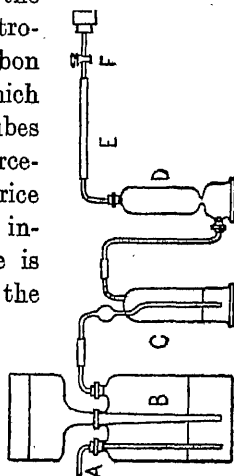



Fig. 7.

stoppers from the effects of the heat two compact rolls of ignited copper gauze, occupying nearly the whole bore of the tube, are inserted, one near the exit end, the other at the entrance. The exit end of the tube is connected with the U tube, H, which is packed with small pieces of pumice. This is fitted into a reservoir, consisting of a small wide-mouthed bottle, N, closed by a two-holed rubber stopper through the other hole of which passes a tube with a tap, or rubber extension and clip. This reservoir contains a mixture of sulphuric acid and potassium dichromate, which is occasionally forced up over the pumice by blowing down the tap-tube and allowed to subside again. The pumice is by this means kept continually moistened with fresh acid and efficiently dries the gases passing through it, while at the same time eliminating sulphur dioxide and trioxide. The carbon dioxide is absorbed in the stoppered weighing tube, J, the left hand limb of which is packed with soda lime or coarsely powdered caustic soda, the other containing calcium chloride. The safety wash-bottle, L, contains potash solution, and K is a guard tube filled with calcium chloride.

To carry out the determination a supply of oxygen is passed into A, tap F closed, and the furnace heated to a bright red. About 1000° C. is the right temperature. The weighing tube, filled with oxygen, is attached and a blank determination carried out by passing a stream of oxygen for half an hour. The flow of gas is regulated by one of the taps on the weighing tube, and the bubbles should succeed one another in the safety wash-bottle, L, without an appreciable pause.

If the blank is satisfactory—it should be zero—2·727 grm. of the sample, sifted through a 30-mesh sieve, or 5·454 if the carbon is under 0·2 per cent, are weighed into a small stoppered weighing bottle containing about 1 grm. of ignited alumina, shaken up, and transferred to the combustion boat. The object of the alumina is to prevent globules of oxide forming round unburnt steel and preventing complete combustion. Red lead, bismuth trioxide, and other oxygen-containing materials have been recommended, but are unnecessary if the temperature of the furnace is high enough, except in the case of some chromium steels. These materials also usually introduce a blank. The combustion boat should be capacious and of porcelain, fire-clay, or alundum. If made of porcelain, it must be covered internally with a coating of thin wet asbestos paper and thoroughly ignited in a muffle. If this precaution is not taken a new boat will probably be necessary for each combustion, since glazed porcelain is attacked by the oxide, which also adheres so firmly as only to be removed with great difficulty without breaking the boat. Alundum boats are very satisfactory, especially when used with the specially prepared alumina which the makers supply. The boat and contents are now quickly inserted into the heated combustion tube, pushed up into the hot part, the protective screen of copper gauze placed in position, and the stopper replaced. The oxygen supply is turned on through the tap, H, and the stream regulated as before. By this means the whole apparatus as far as the tap on the weighing tube is kept under a slight positive pressure of oxygen and the drillings are automatically supplied

with as much oxygen as they require, while there is no possibility of "sucking back." Oxygen from the cylinder may be passed meanwhile into the reservoir to replace that used up. The apparatus needs no watching, and after thirty minutes the weighing tube is removed and re-weighed. It may be re-attached for a further period, but seldom increases further in weight. The increase in weight multiplied by 10 or 5 corresponds to the percentage of carbon, if 2·727 grm. or 5·454 grm. respectively were taken. The combustion boat is then drawn out of the tube and its contents quickly shaken out, another boat being introduced and the next determination made.

Special Steels. Where a steel is only burnt with difficulty under the above conditions, the aid of red lead must be called in to ensure complete combustion. The sample is shaken with a weighed quantity of red lead, in place of the alumina, in a weighing bottle before placing in the boat. A covering of asbestos in this case is essential, as otherwise the litharge formed will creep over the edges of the boat and damage the tube. A blank determination with red lead only present must be carried out, but with good samples this is very low.

The Wet Combustion Method. The method depends on first separating the carbonaceous constituents from the iron by solutions of copper salts and afterwards burning the residue.

A solution containing 250 grm. crystallized copper sulphate and 100 grm. pure ammonium chloride per litre is prepared. The drillings are weighed out in 5·454 grm. lots into marked conical flasks and then

80 c.c. of the solution are added to each. The flasks are shaken round well and allowed to stand overnight. In the morning the residual copper is brought into solution by adding 20 c.c. of hydrochloric acid to each and warming to about 50° C. with occasional shaking. The carbon is then filtered off through ignited asbestos and washed with hot water. The filter pad is carefully lifted out and placed in a marked combustion boat, the sides of the funnel being carefully cleaned by wiping with

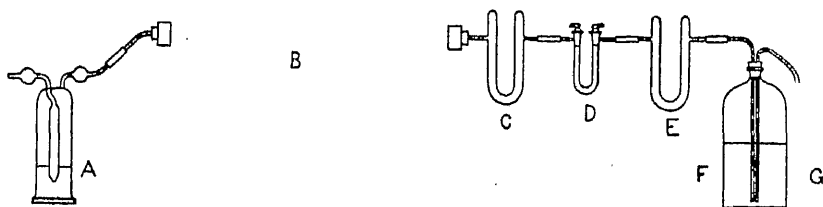



Fig. 8.

small pads of ignited asbestos, and these are also added to the boat. The whole is now dried in a steam or air oven at about 100° C. When dry it is transferred to the combustion tube, which is shown in Fig. 8. This apparatus is similar in most respects to that used in the direct combustion method, but oxygen is unnecessary. Air is drawn through the apparatus at a suitable rate by the aspirator, G. No other purification of the entering air is necessary beyond bubbling through a strong solution of potash in the washer, A. To the other end of the combustion tube are attached a drying tube, C, containing pumice moistened with sulphuric and chromic acids, the weighing tube, D, filled in the

same way as for the estimation by direct combustion, and a guard tube, E, of calcium chloride. The combustion of the carbonaceous matter is generally complete in less than half an hour.

Of other methods for the estimation of carbon, Wüst's method as used by Stadeler (*Metallurgie*, VIII, p. 268) consists in burning about half a gram of the steel mixed with five times its weight of an alloy of antimony 3, tin 1, in oxygen at 900° C., and is stated to be very useful with refractory alloys. Goutal (*Revue de Met.*, 1911, VIII, p. 391) burns in a calorimetric bomb in compressed oxygen, absorbing the carbon dioxide in baryta and titrating the excess of alkali with acid and phenol phthalein, but neither of these methods is likely to find a wide technical application.

CHROMIUM

Chromium occurs in traces in many steels and irons accidentally, owing to its presence in the ores, and is also added purposely to many special steels, particularly armour-plate and high-speed steels. It may be estimated gravimetrically as chromium phosphate, but the volumetric estimation depending on the oxidizing properties of chromic acid is more convenient and generally more accurate. Where traces of chromium only are present, it is best to separate all the chromium first as phosphate and then estimate volumetrically after conversion into chromic acid.

Qualitative Detection. If chromium is present to the extent of 0·5 per cent. or more in a steel, the solution in dilute sulphuric acid will have a pronounced green colour, the solution of a plain steel being practically colourless. Nickel produces the same effect in a much less marked degree.

Gravimetric Estimation. Dissolve 2 grm. of the steel in 40 c.c. hydrochloric acid (1 : 1) and dilute to 200 c.c. Heat the solution and nearly neutralize it with sodium carbonate. When only feebly acid, add 20 c.c. of 10 per cent. sodium phosphate and 10 grm. of sodium thiosulphate. Boil well and allow to settle. Filter through a close filter and wash with 5 per cent. ammonium nitrate solution. Re-dissolve in hydrochloric

acid and repeat the precipitation as before. The precipitate will then be free from iron and manganese, but will contain aluminium, copper, and nickel if present. If absent, ignite and weigh as chromium phosphate containing 40·94 per cent. Cr. The same excess of sodium phosphate should be added in the second precipitation, otherwise a precipitate of uncertain composition will result. If the above metals are present the precipitate must be fused with sodium carbonate, extracted with water and filtered. Aluminium and chromium are present in the filtrate. Acidify with dilute HCl and add dilute ammonia to precipitate the aluminium. Filter, acidify, reduce the chromic acid with sulphurous acid, and precipitate as above. This method should only be used for small amounts, 0·2 per cent. and less, of chromium, and even in this case it is better to fuse the precipitate with sodium carbonate and titrate the chromic acid resulting.

Volumetric Estimation. Weigh 2 grm. of the sample into a 600 c.c. long beaker and add 30 c.c. of water, followed by 15 c.c. strong sulphuric acid. Dissolve with the aid of gentle heat on the hot plate with the cover on. The speed of solution varies considerably with different samples, and may even take some hours. Crystals of ferrous sulphate should be re-dissolved with a little water if they form, otherwise solution will be much retarded. When all is dissolved except a few floating black specks, add 1·2 nitric acid drop by drop from a pipette until all the iron is oxidized, and boil off nitrous fumes. Add 200 c.c. of hot water and then 7 c.c. of 3 per cent. potassium permanganate solution and a small piece of firebrick about the size of a pea to

prevent bumping. Boil for fifteen minutes. A precipitate of manganese dioxide should remain. Now add 50 c.c. of dilute hydrochloric acid (30 c.c. strong acid per 100 c.c.) and boil till the precipitate just clears up. Dilute at once with hot water to 400 c.c. and boil rapidly for half an hour, adding water if necessary to prevent the volume falling below 350 c.c. Allow to cool completely, add a slight excess of ferrous sulphate and titrate back with standard bichromate solution (1 c.c. = ·001 Cr.—*see* Appendix I). The number of cubic centimetres of bichromate equivalent to the total ferrous sulphate added, less the amount taken up in the back titration, divided by 20, represents the percentage of chromium in the sample.

Rapid Volumetric Estimation. The following method—due to Gregory (*Journ. Chem. Soc.*, 1907, p. 1847)—gives accurate results and takes less than an hour.

Dissolve 2 grm. of the steel in as little 1·2 nitric acid as possible, dilute to 50 c.c., add 1 grm. of silver nitrate and 10 grm. of ammonium persulphate and boil for a few minutes. Ammonium chloride (·25 grm. or 2·5 c.c. of 10 per cent. solution) is added—the quantity being insufficient to precipitate the whole of the silver nitrate—and the solution boiled, when the permanganate is destroyed and the manganese partly precipitated as hydrated oxide and partly converted into manganous chloride. The solution is filtered through asbestos after making up to a definite volume, and an aliquot part titrated with ferrous sulphate and standard bichromate. The presence of free silver nitrate throughout the estimation ensures the absence of free chlorine.

Vanadium. In the volumetric estimation vanadi
only interferes by oxidizing part of the excess of ferr
sulphate added. On subsequently titrating back w
bichromate an uncertain end point is obtained bef
enough has been added to oxidize the excess of ferr
sulphate present. If the back titration is carried
with permanganate and the end point taken as reacl
when a slight pink colour does not disappear in hal
minute, the interference of the vanadium is avoic
as the hypovanadate is re-oxidized by the perm
ganate to exactly the same extent as it was produ
by the ferrous sulphate.

Molybdenum and Titanium. These elements do
interfere with the volumetric estimation.

Tungsten. If the sample dissolves but leaves
residue of tungstic oxide, this should be filtered
after oxidizing the iron with nitric acid. If gr
difficulty in effecting solution is encountered, dissol
the sample in hydrochloric acid with a little nitric a
(*see Tungsten*, p. 92), afterwards diluting and separati
the tungstic oxide. Add to the filtrate 15 c.c. of stro
sulphuric acid and evaporate till fumes are free
evolved. Cool, dilute, add permanganate, and proce
as in the ordinary volumetric estimation, adding
necessary a little more permanganate.

COBALT

Cobalt is one of the most recent additions to the ranks of elements specially added to high-speed steels. Its estimation has in consequence not so far received very much attention, but the following methods have been found by the author to work well.

Cyanometric Estimation. This is carried out in the same way as for nickel until the iron has been separated and the 500 c.c. of solution for the titration obtained. At this point it is desirable to add 50 c.c. of 20 per cent. ammonium sulphate solution, as it improves the colour of the solution and adds to the sharpness of the end point. This is slightly more difficult to see than in the case of nickel, as the turbidity appears more slowly, and different operators are liable to take slightly different points. For this reason a standard cobalt solution containing about the same amount as the sample should be added to a solution of a cobalt- (and nickel-) free steel and the potassium cyanide standardized by carrying through the estimation in exactly the same way. One atom of cobalt is, roughly, equivalent to five molecules of potassium cyanide. A standard solution of cobalt is prepared by dissolving about the right quantity of any pure cobalt salt in 1 litre of water, evaporating an aliquot part to dryness with slight excess of sulphuric acid in a

tared dish, heating just to dull redness, and weighing as $CoSO_4$.

Gravimetric Estimation. The estimation of cobalt in high-speed steels is best carried out as follows. Five grams, or less, of the steel are weighed and dissolved in 80 c.c. strong hydrochloric acid as far as possible. Strong nitric acid is then added in just sufficient quantity to dissolve the iron and effect solution. The solution is then evaporated until tungstic oxide begins to separate, diluted with 80 c.c. of hot water, and boiled. The tungstic oxide is filtered off and the solution diluted to about 200 c.c. with hot water. Ammonium carbonate is now added until a permanent precipitate is just formed, which is cleared up by adding 10–15 c.c. acetic acid. The solution is then diluted to nearly 500 c.c. and heated to boiling. Ammonium acetate solution (*see* Appendix I) is added to the extent of 1 c.c. per gram of steel and the solution just boiled, made up exactly to 500 c.c. at the boiling temperature, and 250 c.c. filtered off. To the filtrate, which must be free from iron, 10 grm. of ammonium chloride are added and then ammonia till feebly alkaline. Sulphuretted hydrogen is now passed for about ten minutes until all cobalt, and nickel if present, is precipitated as sulphide together with a small quantity of manganese if much was originally present. The precipitate is allowed to settle, filtered off on pulp, and then washed with 2–3 per cent. acetic acid containing sulphuretted hydrogen, which removes practically all the manganese sulphide. The precipitate is now ignited, and if cobalt only is present, may be converted into cobalt sulphate by moistening with strong nitric acid and a few drops of sulphuric acid

in a tared dish. This is then evaporated to dryness, the sulphuric acid carefully driven off by heating just to dull redness and weighed as $CoSO_4$ containing 38·04 per cent. of cobalt.

If nickel is also present the precipitate is ignited and dissolved in nitric acid and taken to fumes with a small quantity of sulphuric acid as before, and is then dissolved in about 50 c.c. of water. Ammonium sulphate (10 c.c. of 30 per cent.), 100 c.c. 1 : 1 ammonia, and 100 c.c. of water are added and the solution electrolysed between platinum electrodes in a beaker. A current density of about 0·6 ampère per 100 sq. cm. of cathode surface at 3 volts is necessary, and precipitation is complete in about four hours. A trace of MnO_2, if manganese has not been completely eliminated, may separate towards the end of the electrolysis but will not interfere. The precipitated cobalt and nickel are weighed together, dissolved in a little nitric acid, and taken to dryness with excess of hydrochloric acid. They are then dissolved in 100 c.c. of water faintly acidified with HCl per 0·1 grm. of metals. The solution is neutralized with ammonia, acidified with one drop of HCl, heated to 60° or 70°, and the nickel precipitated by adding slight excess of a 1 per cent. alcoholic solution of dimethylglyoxime. Ammonia is then added just to alkalinity, the precipitate filtered off, washed with hot water, dried, and either weighed as $C_4H_{14}O_4N_4Ni$ containing 20·31 per cent. Ni or ignited at the mouth of the muffle and weighed as oxide NiO, cobalt being estimated by difference.

COPPER

Copper, although seldom intentionally added to steel, is usually present in small and varying amounts. If present in fair quantity it may be detected by dissolving the steel in nitric acid, adding dilute ammonia, and filtering, when the filtrate is coloured blue. Nickel and cobalt both interfere with the test, and it is of no great sensitiveness. If traces only are being looked for it is better to carry through an estimation.

Estimation. Weigh 10 grm. of steel into a 600 c.c. beaker, add 75 c.c. of water and then 25 c.c. of strong sulphuric acid, and heat gently till all is dissolved. Dilute to about 400 c.c. with hot water and add 10 grm. of sodium thiosulphate. Boil the solution until the precipitated sulphur clears up, and filter through pulp. The precipitate consists of cuprous sulphide, together with the sulphides of antimony, arsenic, and molybdenum if present, and also possibly the oxides of aluminium, silicon, chromium, and iron. The simplest way to estimate the copper in the mixture is to dissolve the precipitate as far as possible in a little 1·20 nitric acid and estimate the copper colorimetrically after addition of ammonia, and filtration if necessary, by comparison in colour carbon tubes with a standard copper solution. An alternative method of dealing with the precipitate is the following: Ignite and weigh

the precipitate, transfer it to a small beaker, dissolve as far as possible in 10 c.c. strong hydrochloric acid, dilute, and add ammonia till alkaline. Filter off, wash, and ignite the precipitate and subtract its weight from the previous weight. The difference may be taken as representing the weight of cuprous sulphide, which multiplied by 0·798 gives the weight of copper present, but this assumption is liable to grave inaccuracy if arsenic, tin, and particularly molybdenum are present.

Tungsten. This is the only element which interferes seriously with the colorimetric method given above. If present the estimation is much more laborious, but may be carried out as follows: Dissolve 10 grm. of the sample in 50 c.c. strong hydrochloric acid, and when the reaction slackens add drop by drop just enough strong nitric acid to produce a clear solution. Evaporate till a precipitate commences to form, then dilute with 100 c.c. hot water and boil. Filter off the precipitated tungstic acid and silica. Add a considerable amount of sulphurous acid and boil off the excess. Treat the warm solution with a rapid stream of sulphuretted hydrogen until the precipitate of copper sulphide becomes dense and settles readily. Filter and wash the precipitate alternately with water containing sulphuretted hydrogen and 5 per cent. hydrochloric acid. Dissolve the precipitate off the paper with hot 1·20 nitric acid, perforate the filter, and wash through any residual sulphur. Boil until the solution is clear. The estimation may now be finished by the colorimetric method after adding ammonia, or the copper may be estimated iodimetrically in the following way: Add caustic soda or sodium carbonate to the thoroughly

boiled nitric acid solution till a permanent precipitate is produced. Re-dissolve this with a few drops of acetic acid, cool, add about 1 grm. of potassium iodide dissolved in a little water, and titrate the liberated iodine with standard thiosulphate (*see* Appendix I) after adding starch solution.

HYDROGEN

HYDROGEN occurs in appreciable amounts in practically all steels and irons, electrolytic steel being stated to contain sometimes many times its own volume. The presence of hydrogen is most clearly demonstrated by heating the drillings *in vacuo,* after maintaining them *in vacuo* with a drying agent for long enough to remove all moisture, and analysing the gases given off. On account of the very low density of hydrogen the percentage by weight is very small, even when considerable volumes of hydrogen are obtained as above. Thus if a steel yield its own volume of hydrogen the percentage by weight indicated is only slightly over 0·001. It is exceedingly unlikely that such a small proportion of any element can have much injurious influence on the quality of the steel, but in view of the accusations which have been brought against this element, and also for the sake of completeness, the following method of estimation is given.

Estimation. The determination of hydrogen is carried out by burning the steel in dry oxygen and weighing the water formed.

A silica combustion tube, similar to that used in the estimation of carbon by direct combustion, is fitted with two tight one-hole rubber stoppers and placed in a furnace capable of attaining a temperature of at least

900° C. The steel—50 grm. or even more—is weighed out, mixed with a little recently ignited alumina, which must be stored in a good desiccator, and introduced into the combustion tube in recently ignited boats similar to those used in the estimation of carbon. A supply of oxygen from a cylinder, purified in the same way as for carbon determination, but passing through a drying tube of phosphorus pentoxide in addition, is put in connection with the tube, a glass tap on capillary tube being placed close to the rubber stopper. Arrangement must also be made for the supply of pure dried air. The rubber stopper at the other end carries a wide glass tube about $\frac{1}{4}$ in. in diameter, and to this is connected by close-fitting pressure tubing the weighing tube. The weighing tube consists of a straight tube, about $\frac{1}{2}$ in. in diameter, terminating at either end in tubes about $\frac{1}{4}$ in. in diameter and $\frac{1}{2}$ in. long, and during weighing is protected by small glass caps which slip over the open ends with as little clearance as possible. It is filled with phosphorus pentoxide after first pushing a small plug of glass wool down to the end of the wide part remote from the furnace, but the end close to the furnace must not contain glass wool. A guard tube of phosphorus pentoxide, consisting of a U-tube with side arms and with the wide openings of the limbs sealed off, is attached after the weighing tube.

The estimation is carried out as follows : The sample is placed in the combustion tube, which is then swept out for five minutes with pure dried air. The tap on the entrance tube is then closed and the combustion tube, weighing tube, and guard tube evacuated by means of a Fleuss or other pump attached to the guard tube

until the pressure is reduced well below 1 mm. of mercury. The apparatus is allowed to stand empty for half an hour, at the end of which time it is examined for leaks, which are readily shown by a manometer. If none are present, the apparatus is filled again with dry air and the same process repeated twice. This step completely removes moisture from the drillings and apparatus, which is absolutely essential. The author is unaware of any other method of satisfactorily accomplishing this end, mere passage of a current of dry gas for long periods being quite ineffectual. The tube is now allowed to fill up with air, the guard tube removed, and the cap placed on the adjacent end of the weighing tube while the current is still passing. The weighing tube is then disconnected and the other cap quickly attached. The tube issuing from the combustion tube is closed with a rubber cap while the gas is still issuing, and the current of air then stopped. The weighing tube is then carefully polished with chamois leather, weighed, and re-attached as before, followed by the guard tube. The current of oxygen is now admitted at about the same rate as in carbon determinations, the combustion tube heated and kept hot until all the steel is burnt, when it is allowed to cool, the current of oxygen being replaced by air as soon as the combustion is complete. After passing for a further half-hour the weighing tube is removed and re-weighed. The increase represents the weight of water formed, which divided by nine represents hydrogen. A blank estimation should be carried out to ensure the freedom of the oxygen and air from hydrogen, but the blank should not yield more than half a milligram increase in weight.

MANGANESE

METHODS for the estimation of manganese are very numerous, and the results obtained by most of them are so reliable that the task of selecting the "best" method is very difficult. For plain steels the volumetric methods using sodium bismuthate or ammonium persulphate are widely used and reliable, and the former method may even be used for spiegeleisen or ferro-manganese, if suitable precautions are taken, though the gravimetric estimation after separation of the iron as basic acetate is to be preferred. The estimation with sodium bismuthate is interfered with by vanadium, and to a less extent by chromium, but approximate results may be obtained by its use even in the presence of considerable amounts of these metals. Where the greatest accuracy is desired when these elements are present, they must first be removed, one of the simplest methods being that depending on the treatment of the nearly neutral solution with cadmium carbonate, barium carbonate, or zinc oxide, when chromium and vanadium are precipitated and manganese remains in solution. If the steel can be dissolved in nitric acid the manganese may be separated as an oxide approximating to MnO_2 by the addition of small amounts of potassium chlorate and boiling. This precipitate always contains small quantities of foreign matter, and should be dissolved in

1·2 nitric acid containing a little sulphurous acid, and the manganese estimated by the bismuthate method.

Gravimetric Estimation. This estimation, than which none goes more smoothly when skilfully carried out, probably needs more manipulative ability and experience than any other. Dissolve 5 grm. of steel in 30 c.c. of hydrochloric acid and 30 c.c. of water, and when all is dissolved oxidize the iron by adding 5 c.c. strong nitric acid. Dilute the solution to about 250 c.c. with hot water, and cautiously add ammonia until the colour deepens considerably, and then ammonium carbonate until the colour of the solution changes to a deep red, showing that the free acid has been neutralized and that the solution contains basic ferric chloride. Now add the reagent in small quantities until a permanent precipitate is just produced, clear this up with the least possible amount of hydrochloric acid and heat to boiling. Now add 10 c.c. of ammonium acetate solution (33 per cent. acetic acid neutralized with strong ammonia), just boil, and make up to 500 c.c. at the boiling temperature in a graduated flask. Allow the precipitate to settle, and filter through a large dry fluted filter paper into a dry flask. Take 250 c.c. in a graduated flask at the boiling-point and cool under the tap until quite cold. Transfer to a litre flask and add 2 or 3 c.c. of bromine, shake up, add a moderate excess of ammonia, heat to boiling, and maintain near boiling-point for a few minutes. The manganese is precipitated in black flocks which are readily filtered off. Wash the precipitate with hot water, collecting the washings in another beaker apart from the main filtrate, as sometimes the pre-

cipitate has a tendency to run through. If this happens the turbid washings should be re-filtered through pulp or a very fine filter paper, and the residue finally added to the main precipitate. Both are now ignited in a hot muffle, and the residue weighed as Mn_3O_4, containing 72·05 per cent. Mn. Allowing 5 c.c. for the volume of precipitate in half the solution, the percentage of manganese is found from the relation

$$Mn = \frac{\cdot 7205 \times W}{\frac{255}{500} \times 5} \times 100\ \%.$$

The chief difficulties in the method are the complete separation of the iron and the manipulation of rather large precipitates and volumes of solution. The efficiency of the iron separation depends on the exactitude of the neutralization before adding the acetate; ammonia should be added until the solution is so deeply coloured that it is only possible to see through it with difficulty. The final precipitate should always be tested for impurities, of which ferric oxide and nickel are the most likely, although alumina and oxides of copper, nickel, and chromium may also be present. There is no need to fear the inclusion of manganese in the iron precipitate; one precipitation effects a complete separation when properly carried out.

Estimation with Sodium Bismuthate. 1·1 grm. of the steel are weighed into a 200 c.c. conical flask and treated with 30 c.c. of 1·2 nitric acid and heated. When the brown fumes are all driven off, sodium bismuthate is added in small quantities until a pink colour or a precipitate of manganese dioxide persists after five minutes' boiling. The flask is then removed, the solution cleared

up by adding a few drops of sulphurous acid solution, and finally made quite cold under the tap. A small excess of sodium bismuthate is now added, the flask shaken and allowed to stand for a minute or so, and the contents filtered through a thick pad of ignited asbestos. This step presents the most opportunity for error, as it is difficult to see whether the darkly coloured solution is really clear after filtering, and any bismuthate which passes through will seriously affect the result. The filter is washed with 2 per cent. nitric acid until the washings are colourless. A measured slight excess of roughly decinormal ferrous sulphate is now added, and the excess at once titrated back with decinormal permanganate. The total amount of permanganate equivalent to the ferrous sulphate added, less that employed in the back titration, represents the amount equivalent to the manganese in the steel. 1 c.c. of $\frac{N}{10}$ permanganate = ·00110 grm. Mn or 0·1 per cent. on 1·1 grm.

Estimation with Ammonium Persulphate. Weigh into a 6 in. by 1 in. boiling tube 0·25 grm. of the sample, add 10 c.c. 1·2 nitric acid, heat to boiling, and boil till all brown fumes are gone. Cool under the tap and add about 10 c.c. of silver nitrate solution (1 grm. per 1000 c.c.). Now add about 1 grm. of pure ammonium persulphate and heat to boiling. The manganese is oxidized to permanganate, and the excess of persulphate begins to decompose with a copious evolution of oxygen. Cool quickly under the tap before all the persulphate is decomposed, otherwise the manganese may be precipitated as hydrated oxide. Transfer the

liquid to a small conical flask and titrate with sodi arsenite solution (6·94 grm. As_2O_3 and 35 grm. hydrous sodium carbonate per 2 litres). The titrat is carried on until the colour changes to a pale gre but different workers use slightly different end poi for which reason the arsenite solution should standardized against a steel of known, roughly eq manganese content. The percentage of manganese then readily calculated from the relation of the amoun arsenite added to the amount required by the standa

Mechanicalized Method. Messrs. Ridsdale's mo fication of the persulphate method * is arranged permit of adding the silver nitrate and persulphate e in tablet form—a considerable advantage in the case persulphate. It is exceedingly simple and reliable a consists in the following steps :

Weigh 0·2 grm. of sample (0·1 grm. if Mn is o 0·40 per cent.).
Place in test-tube and add 10 c.c. nitric acid (1·1(
Place in vessel of boiling water, as in colour carl determination, till dissolved.
Add one No. 8A tablet, and when dissolved
Add one No. 8B tablet.
Boil exactly one minute from first appearance of a pi
Cool and titrate with arsenite or compare colour w standard.

If manganese appears very high, 10 c.c. of water a another No. 8A and No. 8B tablet may be added af the first.

* *Journal of the Iron and Steel Institute*, 1911, i, 332; elsewhere.

Chromium. Chromium steels, even when vanadium is also present, yield approximate results by the bismuthate method as described above, but owing to the slow oxidation of chromium to chromic acid, results are always a little high and the error increases with the time during which the solution remains in contact with the bismuthate. A certain amount of difficulty is often experienced in dissolving chromium steels. If the steel will not dissolve in 30 c.c. 1·2 nitric acid completely, the addition of 20 c.c. more hot water may be tried. If this is ineffective, the steel may yet dissolve if a fresh quantity is treated with 20 c.c. of water and 30 c.c. of 1·2 nitric acid. If the steel still will not dissolve, the addition of 10 c.c. of 1 : 3 sulphuric acid may help matters; but if even this fails, a fresh quantity must be weighed out and opened out by prolonged gentle heating with about 10 c.c. of 1 : 3 sulphuric acid. Solution will be very much retarded if crystals of ferrous sulphate are allowed to separate. Hydrochloric acid must not be employed, as it decomposes the bismuthate.

In whatever way the steel is got into solution, at least 30 c.c. of 1·2 nitric acid must be present and the volume not much over 40 c.c. The bismuthate estimation is then carried out as usual.

For the greatest accuracy the manganese and chromium should be separated. The basic acetate separation is not interfered with by chromium, but it is quicker to employ the chlorate method. For this separation both hydrochloric and sulphuric acids must be absent, and if the steel cannot be dissolved by nitric acid alone the sample should be dissolved in 6 c.c. of strong nitric acid together with 4 c.c. of hydro-

chloric acid in a 400 c.c. beaker, and after evaporating just to dryness evaporated twice more with nitric acid to remove the hydrochloric acid. The residue is then taken up with 20 c.c. strong nitric acid, or if the sample was originally dissolved in nitric acid alone the solution is evaporated to low bulk and 20 c.c. strong nitric acid added. About 4 grm. of potassium chlorate are now added in small quantities to the boiling solution. The manganese separates out as peroxide. The solution is thoroughly boiled after adding the last of the potassium chlorate, filtered, after cooling, through ignited asbestos, and the precipitate washed three times with strong nitric acid. If the nitric acid contains nitrous acid this must be eliminated by boiling, or prolonged aspiration of air, otherwise loss of manganese through reduction will occur. The precipitate, which may contain a number of impurities in small amounts, is now dissolved from the filter by passing through in small quantities 30 c.c. of 1·2 nitric acid containing a little sulphurous acid. The solution is now boiled and the estimation finished as in plain steel, except that there is no need to add bismuthate to the boiling solution.

Vanadium. In the bismuthate estimation when ferrous sulphate is added to reduce the permanganate, the vanadium, which is present as vanadate, is also reduced to the blue hypovanadate, and this is only slowly re-oxidized by permanganate in the cold, which makes the exact end point a little doubtful, and the solution, of course, must not be heated or the nitric acid present will react with the ferrous sulphate. The estimation, however, is quite practicable, and is to be recommended on account of its simplicity if not much

vanadium is present. The gravimetric method is also applicable, but if vanadium is high some difficulty may be experienced in getting the neutralization point before precipitating the iron, as a brown precipitate containing both iron and vanadium is formed. This should not be re-dissolved, but the estimation proceeded with, taking care to add only a small excess of acetate. If chromium is also present, or if the vanadium content is high, it is desirable to separate manganese as follows: The sample (2·2 grm.) is brought into solution in nitric acid, or nitric acid containing a small quantity of sulphuric acid, in one of the ways mentioned under Chromium (*supra*). The solution is nearly neutralized with sodium carbonate and transferred to a 50 c.c. graduated flask. A sufficient quantity of fairly thick cream of cadmium carbonate or zinc oxide with water is added to neutralize the remaining acid and leave a slight excess after precipitating the chromium and vanadium. The solution is diluted to the mark with water, shaken up, and allowed to settle. After filtering through a dry filter into a dry flask, 25 c.c. of the filtrate are extracted with a pipette previously rinsed out with the solution, and transferred to a 200 c.c. conical flask. Strong nitric acid (17 c.c.) is added, the solution cooled, and the estimation proceeded with by adding sodium bismuthate, filtering, and titrating as in steel. 1 c.c. of $\frac{N}{10}KMnO_4$ = 0·1 per cent. Mn if 2·2 grm. was originally taken.

Titanium. With small amounts of titanium any of the methods for plain steel may be used. With ferro-titanium some difficulty of solution in nitric acid may

be experienced, but the addition of a few drops of hydrofluoric acid produces perfect solution, and the estimation is then carried out as in steel, with sodium bismuthate. The amount of hydrofluoric acid added should be only just enough to effect solution, as otherwise the bismuthate oxidation will be interfered with.

Tungsten. Tungsten does not interfere with the bismuthate method of estimation in steel, but with high manganese content a separation, preferably by the chlorate process, must be made. If hydrofluoric acid has been used in effecting solution of the alloy, results by the bismuthate method may be irregular. In this case it is best to remove hydrofluoric acid by evaporation with sulphuric acid, but not more than 3 per cent. by volume of sulphuric acid must be present in the solution oxidized by bismuthate.

Spiegel and Ferro-Manganese. Manganese may be rapidly and satisfactorily estimated in these alloys by the bismuthate process, if precaution is taken to have plenty of nitric acid present and too large a weight of the sample is not taken. The commonest cause of failure in the estimation is the decomposition of the permanganate after formation into a brown iridescent scum, consisting essentially of peroxide of manganese, which is filtered off with the excess of bismuthate. This trouble can be avoided if the following details are used. Dissolve 0·22 grm. of spiegel in 50 c.c. 1·2 nitric acid, destroy organic matter, and reduce any peroxide formed with bismuthate as in steel. Cool, add bismuthate, filter through asbestos into a flask containing 50 c.c. of water, and finish in the ordinary way. 1 c.c.

$\frac{N}{10}$ $KMnO_4$ = 0·5 per cent. Mn. With ferro-manganese the weight taken should be about one-fourth that of spiegel. This is best arranged for by weighing 0·22 grm. which is dissolved in 50 c.c. 1·2 nitric acid, and the organic matter oxidized in the usual manner. After reducing any oxidized manganese compounds, the solution is diluted to 100 c.c. with 1·2 nitric acid. To 25 c.c. of this solution 25 c.c. of 1·2 nitric acid are now added, followed by bismuthate, and the estimation finished as usual, 1 c.c. $\frac{N}{10}$ $KMnO_4$ = 2·0 per cent. Mn under the above conditions. It is better to operate as above by taking an aliquot part than to commence with a very small initial weight, chiefly because trouble from want of homogeneity in the sample is lessened, and also because an error of weighing of $\frac{1}{10}$ milligram would not be negligible in this case.

The volumetric method, although quicker, is less accurate than the gravimetric estimation, and the latter is to be recommended when speed is not a prime object. The details are precisely the same as for manganese in steel (above), except that 1 grm. only of the alloy should be taken, and that a little more difficulty in getting the neutralization perfect may be experienced on account of the large amount of manganese and little iron present.

MOLYBDENUM

MOLYBDENUM is frequently present in high-speed steels, its effect being similar to that of tungsten, with which it may easily be confused in analysis. Molybdenum may be readily separated from iron by the well-known method using aqueous caustic soda, and estimated in the filtrate as lead molybdate. If tungsten is present it will be co-precipitated as lead tungstate, and molybdenum and tungsten should be separated by Ibbotson and Brearley's method.

Estimation in the Absence of Tungsten. Dissolve the sample (2 grm.) in 20 c.c. of hydrochloric acid with the aid of heat and oxidize the iron by adding a slight excess of nitric acid. Heat to boiling, dilute to about 100 c.c. with hot water, and neutralize nearly all the free acid with caustic soda, but leaving the solution clear yellow in colour. In another flask heat 40 c.c. of 20 per cent. caustic soda to near boiling and pour the contents of the other flask carefully into the middle of the solution with thorough shaking. Cool and make up to 200 c.c. in a graduated flask, and filter off 100 c.c. through a dry filter. Acidify the filtrate with hydrochloric acid, adding about 5 c.c. excess. Heat, add 20 c.c. of 4 per cent. lead acetate and 50 c.c. of ammonium acetate. Heat to boiling and keep hot for about a quarter of an hour until the precipitate settles well.

Filter off, wash with hot water, and ignite in a weighed porcelain crucible to lead molybdate $PbMoO_4$ containing 26·16 per cent. of molybdenum.

Estimation in the Presence of Tungsten. The following method is due to Ibbotson and Brearley, and gives excellent results. Five grams are dissolved with gentle heating in 90 c.c. of hydrochloric acid *plus* 10 c.c. of nitric acid. The solution is evaporated just to dryness, but the residue must not be baked. The mass is taken up in dilute hydrochloric acid (20 per cent.) and the tungstic oxide and silica filtered off together, all the molybdenum remaining in solution. The tungsten and silica may be washed, ignited, weighed, and separated by hydrofluoric acid if their estimation is required. The filtrate containing the molybdenum is nearly neutralized with caustic soda and the estimation proceeded with as above in the absence of tungsten.

NICKEL

Nickel seldom occurs in steel in appreciable quantities unless specially added. High-speed steels, armour plate, gun steels, and other steels where great toughness is required often contain nickel. High nickel alloys, such as Invar, are commercially useful in view of the smallness of their coefficient of expansion, their slight change in modulus of elasticity at moderate temperatures, and of their magnetic properties.

Qualitative Detection. There is no very simple test for the detection of small quantities of nickel in the presence of large amounts of iron. If a fair amount (4 per cent.) is present, the solution of the steel in dilute sulphuric acid will be distinctly greener than that of a plain steel, but chromium produces the same effect. Amounts down to 0·1 per cent. may be detected if chromium is absent by dissolving 1 grm. of the sample and 1 grm. of a similar steel containing no nickel in about 10 c.c. of strong hydrochloric acid and comparing the colours of the solutions. That containing nickel will be distinctly greener. If there is any tendency to oxidation a little stannous chloride solution may be added without interfering with the test. As many varieties of steel contain traces of nickel, its absence from the standard must be ascertained with certainty. Small amounts may be detected by pouring the nearly

neutral solution in nitric acid into excess of ammonia, filtering and passing H_2S. A blue solution yielding a black precipitate indicates nickel, but copper behaves similarly. The best test is to carry through an estimation, which takes only a short time.

Volumetric Estimation. The volumetric estimation of nickel is to be preferred to the gravimetric as well for its accuracy as for its rapidity. There are many variations in the actual details of the various procedures used, but most depend on adding excess of standard potassium cyanide solution to a neutral or alkaline solution containing the nickel and titrating the excess, after adding a little potassium iodide, with silver nitrate until the appearance of a yellow turbidity of silver iodide indicates that the end point has been reached. Citric acid is sometimes used to keep the iron in solution when ammonia and potassium cyanide are added, but this results in the production of a very dark solution in which the cloud of silver iodide is only seen with difficulty, while if chromium is also present the difficulty is much increased both by the colour and the chemical interference of chromium. The following method is but little, if any, longer than those in which citric acid is employed, and as the final titration is made in a clear colourless solution the end point is much sharper.

Dissolve 1 grm. of the steel in a 600 c.c. flask in a mixture of 6 c.c. nitric acid and 4 c.c. hydrochloric acid. Heat gently until the red fumes clear and only a small amount of clear red liquid remains. Add about 300 c.c. of hot water, and then dilute ammonia (1 : 10) until the free acid is neutralized and the solution takes

on a deep red colour which can only be seen througl with difficulty, but contains no precipitate. Coc completely under the tap, transfer to a litre graduate flask, and run in a measured quantity of standar potassium cyanide, more than equivalent to the nicke present, but avoid a large excess. Add 20 c.c. o ammonia (1 : 1), shake up and dilute to the mark Pour off into a large beaker, cover with a clock glass and allow to stand for a few minutes until the pre cipitated ferric hydroxide has subsided. Pour of exactly 500 c.c. of the clear liquid. If the precipitat has settled well it is quite unnecessary to filter, as th small amount of ferric hydroxide carried forward onl interferes with the subsequent titration in so far as i makes the liquid turbid. Add to the 500 c.c. of liquid contained in a large conical flask, 10 c.c. of 1 per cent potassium iodide solution and run in standard silve nitrate (*see* Appendix I) from a burette until a dro just produces a slight opalescence in the liquid whicl does not disappear. The number of cubic centimetre of silver nitrate equivalent to the total amount o potassium cyanide added, less twice the amount use in the back titration, divided by ten, represents th percentage of nickel in the steel. The potassiun cyanide used should be titrated against the silve nitrate, using the same conditions of dilution an content of potassium iodide and ammonia. It ma also be standardized against a pure nickel solution but the result obtained is identical with that obtaine with silver.

Dimethylglyoxime (or Acetyldioxime) Method This method is particularly to be recommended in th

presence of cobalt, or when small amounts of nickel are to be estimated.

Five grams of the sample are dissolved in hydrochloric acid and the iron separated as basic acetate exactly as in the gravimetric estimation of manganese. The warm filtered solution—which will contain a trace of acetic acid—is transferred to a beaker and about twice as much dimethylglyoxime, 1 per cent. alcoholic solution, is added as is necessary to combine with the nickel (about eight times the weight of nickel present). The solution is thoroughly agitated and the bright red precipitate allowed to settle. The precipitate is filtered off and washed. It may then be either weighed in a Gooch crucible, after drying at 100°, as the nickel salt of dimethylglyoxime, $NiC_8H_{14}O_4N_4$, containing 40·74 per cent. Ni, or ignited to nickel oxide. If the latter course is adopted the precipitate should be ignited gently at the mouth of muffle before raising to a bright red heat. Nickel oxide contains 78·7 per cent. Ni.

Cobalt. Cobalt seriously interferes with estimation of nickel cyanometrically, as it combines with potassium cyanide in the same way as nickel—four atoms of nickel being about equivalent to three of cobalt. The dimethylglyoxime method is not invalidated by cobalt, and should be used if this element is also present.

Chromium. Chromium does not interfere with either of the above methods, but produces serious complications in those modifications of the cyanometric method in which the iron is retained in solution by means of citric acid.

NITROGEN

NITROGEN occurs in very small amounts in all varieties of steel. Its effect on the properties of the metal is very doubtful, but is probably slight, although some metallurgists maintain that it is even more injurious than phosphorus.

No satisfactory method for the estimation of nitrogen has been evolved. The work which has so far been carried out tends to show that great difficulty will be experienced in finding a method of procedure which will estimate the total nitrogen present. The methods so far proposed consist in the solution of the steel in acids, or in solutions of copper salts, followed by estimation of the ammonia formed from the nitrogen present in the steel; or in heating the steel *in vacuo*. Investigation has shown that in the solution methods part of the nitrogen escapes as gas, part is converted into ammonia, and part remains with the residue; while after heating to 1100° *in vacuo*, ammonia can still be detected when the steel is cooled and dissolved in acids. In view of these facts it is evident that no very definite meaning can be given to the value obtained by the following solution method, but it is included as serving to show any variations in amount of nitrogen, and in view of its having been used in a modified form to obtain a considerable number of data on the nitrogen content of steels.

Estimation. A considerable quantity of ammonia-free water is first prepared by distilling ordinary distilled water to which about 10 c.c. per litre of concentrated

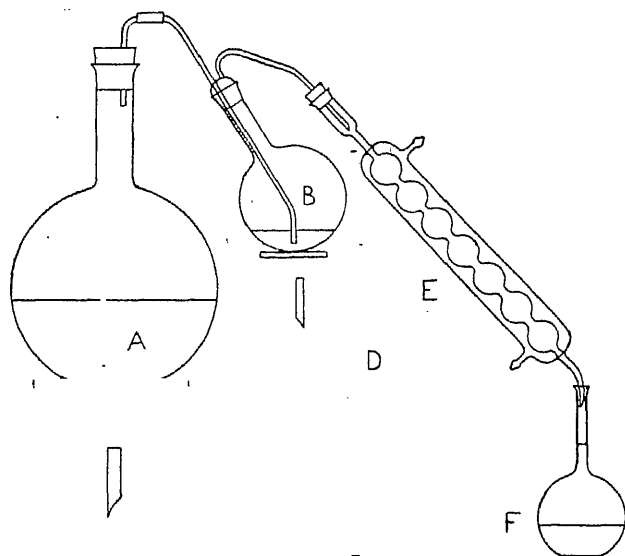



Fig. 9.

sulphuric acid has been added, and is preserved in an accurately stoppered glass bottle.

The sample (1 grm.) is weighed and placed in a 300 c.c. round flask which has previously been well rinsed out with ammonia-free water. Ammonia-free water (10 c.c.) is added, followed by 1½ c.c. strong

sulphuric acid, or 7 c.c. strong hydrochloric acid, a1
the contents of the flask are gently heated until ever
thing is dissolved except a slight carbonaceous residı
The liquid is now transferred to the small flask, B
the diagram, which is closed by a ground joint greas
with vaseline and carries tubes as shown. An ordina
ground-neck wash-bottle is readily converted into
suitable distilling flask. Pure sodium carbonate (40 c
of 10 per cent. solution) is added, the flask quicl
closed and attached, and steam passed through fr
the large boiling flask, A. The distillate, which w
contain all the ammonia, is collected in the 250 c
graduated flask. When just filled to the mark it
removed and a further 50 c.c. is collected in anotl
vessel. This last portion should be free from ammon
but if not the distillation must be continued until
more ammonia comes over. If the additional 50 c
was free from ammonia the contents of the flask a
thoroughly mixed by shaking and 50 c.c. are placed
a Nessler comparison cylinder which has previou
been washed out with the same solution. To anot
Nessler cylinder is added 10 c.c. of a standard nitro
solution (made by dissolving 0·3818 grm. pure ammoni
chloride in 1 litre of ammonia-free water and dilut
100 c.c. of this solution to 1 litre with ammonia-f
water). The cylinder is then filled to the mark w
ammonia-free water and placed beside the other o
white tile. Nessler's solution (2 c.c., *see* Appendi
is now added to each cylinder and the colours produ
compared. If they are unequal in depth another co
parison cylinder must be prepared, using less or m
of the standard solution. It is not permissible to

more of the standard to the liquid already containing Nessler solution, as the colour produced in this way is dissimilar and does not spread evenly through the liquid. When the colour has been matched, the amount of nitrogen standard added is noted, and the percentage of nitrogen calculated. When carried out as above, 1 c.c. of standard = ·005 per cent. N in the sample ; or 1 c.c. of standard = ·00001 grm. N.

A blank determination must be made, as almost any nitrogenous impurity in the reagents will form ammonia when boiled with caustic soda and ferrous hydroxide. The blank is carried out by adding, after a distillation has been completed, the same amount of acid and alkali to the distilling flask as was used in the original estimation.

The apparatus should be thoroughly boiled out for about three hours before an estimation is made, and for part of the time there should be no water in the condenser. This is absolutely essential as the apparatus, particularly the rubber connections, is liable to contain small amounts of ammonia, or other substances, which when distilled in steam yield a brown or yellow colour with Nessler's solution.

OXYGEN

OXYGEN occurs to a greater or less extent in all varietie of steel, but is practically absent from pig and cas iron. Methods for the estimation of oxygen have bee put forward by a number of workers, but until recentl no reliable method—that is to say, no method givin results to which a definite meaning could be assigne —was known, and in consequence statements as t the effect of oxygen on the properties of the steel mus be accepted with considerable reserve. The balance o opinion favours the view that oxygen is distinctl harmful in its effects, producing accelerated rustin and making the metal red-short, but some workers hav held that the presence of oxygen increases the ductilit of the metal. Until further data are available it is im- possible to make any definite statement with certainty

For a discussion of the forms of combination in whic oxygen is present in steel, reference may be made t the author's paper on the "Estimation of Oxygen i Iron and Steel" (Carnegie Scholarship Memoirs of th Iron and Steel Institute, vol. v., 1913, p. 70), where a review of the methods of previous workers on th estimation of oxygen is also given. The conclusio is arrived at that oxygen may be present as carbo monoxide, carbon dioxide, ferrous oxide, manganou oxide, and slag, and also in combination with any

special addition to the steel, such as titanium, aluminium, &c. Evidence is brought forward for the solubility in steel of the first four compounds and the probable insolubility of the remainder, a conclusion which makes it likely that any harmful effects due to oxygen will be produced by the first four. The method about to be described takes account only of oxygen

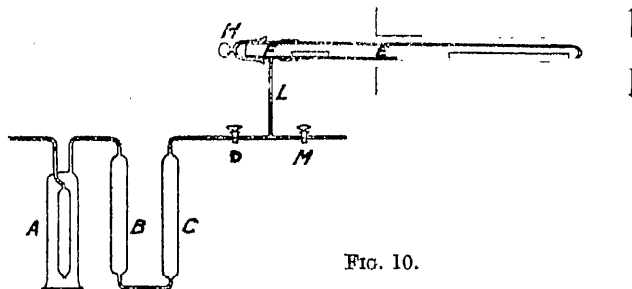



FIG. 10.

combined in these four ways, but as a consequence of this fact is probably of greater usefulness than a method estimating the whole irrespective of its mode of combination.

Estimation. The estimation is performed as follows: Hydrogen free from oxygen is generated in a Kipp's apparatus * (not shown in diagram) by the action on zinc of dilute sulphuric acid (1 : 6), free from nitric acid and oxides of nitrogen, and containing about 5 grm. of crystallised ferrous sulphate per 100 cubic centimetres. The gas is purified by bubbling through strong sulphuric acid in the washing bottle, A, from which it passes to B, containing solid caustic potash, followed by calcium chloride. It is then thoroughly dried by passing through

* The complete apparatus is supplied by Messrs. C. E. Müller, Orme & Co., of 148 Holborn.

the phosphorus pentoxide in C. All rubber connections are rendered perfectly gas-tight by a covering of "Chatterton's compound" or sealing-wax. E is a vitreous silica tube closed at one end, 18 in. long by 1 in. in internal diameter, the walls being 3 mm. thick; it is connected by a gas-tight rubber joint with the glass extension, F. This is of the same diameter, carries a side tube, L, and is closed by a glass cap, H, which fits over the end. The side tube L carries two stopcocks, D and M, on a T-piece. D is connected with the hydrogen supply, and M with a Fleuss pump. The silica tube is held horizontally in a strong clamp in such a manner that an electric furnace can be placed round it for 9 or 10 in. of its length, and can be removed at will without disturbing any part of the apparatus. The steel to be analysed is placed in a nickel boat (previously ignited in hydrogen) and pushed up near the closed end of the tube. The water resulting from the reduction is absorbed by a small glass boat containing phosphoric oxide inserted into the open end of the tube near the glass cap.

To carry out a determination, the silica tube is first completely freed from moisture by carrying out a blank heat with an unweighed boat of phosphoric oxide in the cold end. When cold the nickel boat is taken out and weighed. About 20 grm. of steel are then placed in the boat and the whole is re-weighed. The steel should be in the form of drillings or turnings, and preferably free from moisture—this is readily ensured by keeping the drillings in a desiccator. A small glass boat containing phosphoric oxide is weighed in a special weighing bottle provided with small feet to prevent

rolling on the balance pan. The drillings are now placed in the silica tube near the closed end and a small unweighed boat containing phosphoric oxide placed near the open end. The cap is replaced and the tube evacuated and allowed to remain so for a minute or two, during which time any moisture and air condensed on the drillings are completely removed. Hydrogen is now admitted up to atmospheric pressure, and the weighed boat of phosphoric oxide substituted for the other. While the change is being made, the hydrogen completely escapes from the tube and is replaced by the same volume of laboratory air. A small correction is made for the amount of water vapour introduced in the air, but this never amounts to more than 1 or 2 milligrammes. The tube is now exhausted, filled with hydrogen, and re-exhausted. In order to remove the last traces of air, this washing out with hydrogen may be performed twice. Finally, hydrogen is admitted up to half or two-thirds atmospheric pressure, which is readily effected by arranging that the volume of the purifying apparatus between tap D and the tap on the Kipp's apparatus is from one to two times that of the silica tube and attachment. Then (the purifying apparatus being filled with hydrogen at slightly more than atmospheric pressure) by shutting off the Kipp's apparatus and making connection with the vacuous tube, the latter is filled with hydrogen at the right pressure. The object of this diminished pressure is to prevent the cap being blown off by the increased pressure due to the expansion of the gas on heating. The electric furnace—previously heated to 1000°—is now pushed over the end of the tube until 9 or 10 in.

are surrounded, and allowed to remain there for three-quarters of an hour, or less if the drillings are fine. At the end of this time the furnace is removed and the tube allowed to cool. The cooling is greatly assisted by an air-blast, but this is not essential. When cold it is filled with hydrogen up to atmospheric pressure, tap D closed, the cap removed, and the P_2O_5 boat quickly replaced in the weighing bottle and weighed. The loss in weight of the steel is always slightly greater than the gain of the P_2O_5 boat by reason of the loss of sulphur and carbon. A complete estimation may be carried out in less than an hour, and during most of the time the operator is free to do other work.

In order to determine the amount of moisture introduced when the tube is opened for the insertion of the weighed boat of phosphorus pentoxide, a blank determination must be made. This is done by carrying through a determination as above with no steel in the tube. It is important to introduce the boat *as quickly as possible*, as it rapidly increases in weight when left exposed to the atmosphere. The time occupied in removing the cap, inserting the boat, and replacing the cap should not exceed six seconds, and may be less.

The state of the sample has an important bearing on the result. The most satisfactory form of sample for analysis is turnings of 0·2 millimetre ($\frac{1}{125}$ in.) thickness, or less. In practice, if drillings are clean it is sufficient to sift out the finest part through a 30-mesh sieve and work on these, but in every case the drillings or turnings must be taken with every precaution to ensure absence of scale, rust, and oil; and, of course, the drillings or turnings must not be taken off hot.

PHOSPHORUS

PHOSPHORUS is present to a greater or less extent in all varieties of steel and iron, and in view of its important effect on the properties of the metal its estimation is almost invariably required. Probably more processes for its estimation have been worked out than for any other element, but the differences chiefly consist in variations of the means by which a final precipitate of ammonium phospho-molybdate is obtained and of the further treatment of this compound.

The methods described below are adapted to meet various needs—rapidity, accuracy, or convenience when performing a large number of operations. A single estimation can be made by the permanganate oxidation method in twenty minutes or even less, but although the second method requires nearly a day for a complete estimation a large number can be performed in about the same time as by the other. The slower method is more reliable than the other, chiefly in view of the more satisfactory separation of arsenic, which may, if not removed, under certain conditions be co-precipitated with the phosphorus; and also because very small precipitates of phospho-molybdate separate more quickly and completely when this method is employed.

Quick Method. Dissolve 2 grm. of the sample in 45 c.c. 1·2 nitric acid in a 300 c.c. conical flask and boil

until brown fumes are gone. Now add potassium permanganate solution (3 per cent.) in sufficient quantity to produce a pink coloration or brown precipitate after five minutes' boiling. Remove from the plate, cool somewhat, add just enough sulphurous acid solution to clear up the precipitate, and cool thoroughly. Add ammonia (1 : 1) with gentle swirling of the liquid until the colour begins to deepen but still just remains yellow. Now heat to boiling, remove from the plate, and add at once 30 c.c. of molybdate reagent (*see* Appendix I), shake the flask vigorously, and allow the precipitate to settle. Precipitation is complete almost at once. Filter through a 11 cm. filter paper in a ribbed funnel and wash the flask and paper free from iron salts with nitric acid (20 c.c. per litre), and then wash both flask and filter free from acid with 2 per cent. potassium nitrate solution. Four washes with each, paying particular attention to the edges of the paper, should be enough. Test the washings to make certain all acid has gone, and then transfer the filter and its contents back to the flask, add a measured excess of standard caustic soda (*see* Appendix I), and shake round until all the yellow precipitate is dissolved. Now add a drop or two of phenol phthalein and titrate back with standard sulphuric acid until the colour becomes very faint. The acid equivalent of the caustic soda added, less the acid used in the back titration, represents the amount of acid equivalent to the precipitate, and hence the amount of phosphorus is readily calculated. It is quite safe to assume that 1 c.c. $\frac{N}{100}$ sulphuric acid equals ·001350 grm. P, but for additional security the acid

should be standardized against a steel of known composition. It is generally believed that arsenio- and silico-molybdates tend to come down with the precipitate obtained as above, but the author has been unable to detect the presence of either in any precipitate examined. For percentages of phosphorus under 0·02 the precipitate may only form with difficulty, and in this case the method described below is preferable.

Long Method. Dissolve 5 grm. of the steel in 35 c.c. nitric acid and 25 c.c. hydrochloric acid in an 800 c.c. beaker, and evaporate to dryness and bake. Take up in 40 c.c. strong hydrochloric acid, boiling with the cover on until all is dissolved, and then evaporate just to dryness and take up in about 20 c.c. hydrochloric acid and evaporate to low bulk. Dilute with about 50 c.c. hot water and add pure zinc foil in sufficient quantity to reduce all the iron to the ferrous condition, when the colour of the solution becomes pale green. During this step the arsenic is reduced to the arsenious condition and in great part evolved as arsine, AsH_3. Evaporate as far as possible, thus driving off the remaining arsenic as arsenious chloride. Cool, add 30 c.c. of water and, cautiously, 20 c.c. of nitric acid. Boil till brown fumes are all evolved and transfer to a 600 c.c. conical flask. Add ammonia (1 : 1) until all the iron is precipitated and the brown mass smells strongly of ammonia, then just re-dissolve the precipitate with strong nitric acid, finally adding 4 c.c. excess. Heat to boiling and deliver into the centre of the rotating solution from a pipette 15 c.c. of 10 per cent. ammonium molybdate with constant shaking. All flocks of molybdic acid, if formed at all, should be

immediately re-dissolved. The precipitate, after shaking and standing until the upper liquid is clear, is filtered off, and may be treated as in the preceding method, or in either of the following ways: (*a*) Filter on a smooth filter paper and wash the precipitate in the usual manner, but direct the washings in such a way that the precipitate is all carried down into the point of the filter. Dry the filter at about 120° in an air oven. When dry, open out the filter, brush the precipitate into the balance-scoop, and weigh. If properly performed a negligible amount of precipitate will remain attached to the paper. The weight of precipitate, multiplied by 0·0165, equals the weight of phosphorus in the steel taken. (*b*) The precipitate may be transformed into the equivalent amount of lead molybdate and weighed as such. This is the most satisfactory way of dealing with the precipitate for accuracy, as the precipitate of lead molybdate settles and filters very readily, may be ignited without any unusual precautions, and weighs nearly 150 times as much as the phosphorus from which it results. The flask and filter containing the precipitate are washed free from iron with dilute nitric acid, and the precipitate is then dissolved off the filter with a small quantity of ammonia and returned to the flask, the filter being well washed. Strong hydrochloric acid (10 c.c.) is now added, the solution heated, and then 10 c.c. of lead acetate (4 per cent.) added. In another flask 50 c.c. of 20 per cent. ammonium chloride and 50 c.c. of ammonium acetate are heated to boiling and then the contents of the other flask are added. A white, rather flocculent precipitate of lead molybdate forms, which settles readily if the liquid is kept hot

for a short time. This is filtered off, washed with hot water, and ignited in porcelain in the muffle without drying. The weight, multiplied by 0·007, represents the weight of phosphorus in the amount of sample taken.

Mechanicalized Methods. These methods, recently introduced by Messrs. C. H. and N. D. Ridsdale,* constitute the simplest and most rapid methods at present available. The addition of the reagents in the form of tablets of pure and carefully tested materials, and the standardization of all conditions, lead to a uniformity in results only to be obtained with difficulty by other methods ; while the elimination of the personal element makes possible the utilization of comparatively unskilled labour.

1. *Without Separation of Arsenic.* The sample is dissolved in a measured volume of nitric acid (1·22, of which 25 c.c. neutralize 9·13 grm. pure anhydrous Na_2CO_3), simmered gently, and oxidized with a tablet containing permanganate. Another tablet, containing ammonium chloride, ammonium nitrate, and ferrous sulphate is then added, the liquid simmered till clear, and 10 to 15 c.c. of 10 per cent. ammonium molybdate added. The liquid is next shaken for one minute, allowed to stand for two minutes, the precipitate filtered off, washed, and titrated. The operations are, therefore, briefly :

Weigh 2 grm. of sample.
Dissolve in 31·5 c.c. 1·22 nitric acid.
Simmer for two minutes.

* *Journal of the Iron and Steel Institute*, 1913, i, 332; and elsewhere.

Add one No. 4 tablet.

Simmer for two minutes.

Add one No. 6 tablet and simmer till clear.

Bring to a volume of 50 c.c. in a marked beaker.

Boil, and add 10 to 15 c.c. molybdate solution (10 per cent.).

Shake one minute, stand two minutes. In these circumstances silicon from 0·3 to 0·4 per cent. does not interfere.

2. *Arsenic Separated.** A crude precipitate containing all the phosphorus is first obtained exactly as described above. This is then dissolved in alkali, quickly acidified with hydrochloric acid, and the arsenic reduced with zinc and precipitated as sulphide by adding zinc sulphide. The excess of sulphuretted hydrogen is removed by boiling, re-oxidation effected with potassium chlorate, and the free acid neutralized with sodium acetate. The solution is then suddenly and completely re-acidified with nitric acid, and ammonium molybdate and nitrate added together, when the pure phospho-molybdate separates. The method consequently consists in the following operations :

Weigh 4 grm. of sample.

Dissolve in 62 c.c. of 1·22 nitric acid.

Oxidize with two No. 4 tablets.

Add two No. 6 tablets.

Boil and add 25 to 30 c.c. 10 per cent. ammonium molybdate.

Filter and wash free from iron with cold water.

Re-dissolve in 0·6 grm. pure sodium hydrate.

Add 13 c.c. HCl (1·16).

* *Journal of the Iron and Steel Institute*, 1913, i.

Reduce with one No. 9 talbet.

Precipitate arsenic as sulphide with one No. 10 tablet.

Filter.

Boil off H_2S.

Re-oxidize with one No. 11 tablet.

Neutralize with one No. 12 tablet.

Add a solution of one No. 13 tablet (50 c.c.).

Re-acidify with 7·0 c.c. nitric acid (1·42).

Shake, filter, and titrate as before.

The foregoing descriptions are only to be regarded as outlines. The fullest details of working are issued with the reagents as issued by Messrs. Ridsdale and their agents.*

* See Note on the Estimation of Phosphorus in Steels containing Arsenic, page 103.

SILICON

THE determination of silicon in steel is one of the simplest and most accurate estimations. In high silicon alloys, on the other hand, considerable difficulties have to be overcome, which arise chiefly from the remarkable power possessed by these alloys of resisting attack by reagents. The assistance of hydrofluoric acid cannot, of course, be called in to effect solution for this estimation, and in many cases fusion with alkaline oxidizing agents has to be resorted to. In the presence of tungsten also some difficulty may be experienced. No volumetric method for the estimation of silicon has so far been made use of, the estimation in practically every case depending on weighing the silicon as silica. When steel is dissolved in hydrochloric acid, contrary to the behaviour of aluminium and some other metals, no silicon is lost as silicuretted hydrogen. A certain amount of silicon is always dissolved when steel is dissolved in acids—indeed, with nitric acid of density 1·2 the whole goes into solution—necessitating evaporation to dryness and baking, or else evaporation with sulphuric acid till white fumes are given off, for its complete elimination.

Estimation. This is conveniently carried out in conjunction with the estimation of sulphur (*q.v.*), but

if silicon only is required the following method is quicker: 5 grm. of the steel are dissolved in 40 c.c. of strong hydrochloric acid in a capacious beaker covered with a clock-glass. When all is dissolved the cover is removed and the whole evaporated gently to dryness and gently baked—not on the hottest part of the plate—until the mass is pinkish brown. The beaker is removed and cooled, about 40 c.c. of strong hydrochloric acid added, followed by about 200 c.c. of hot water when all is in solution. The solution is then filtered and the whole of the precipitate carefully transferred to the filter with the help of a rubbered rod. The filter paper is washed, particularly at the edges, alternately with hot water and dilute hydrochloric acid, until completely free from iron. It is then ignited, and the precipitate brushed out and weighed. Where there is any reason to fear contamination the ignited precipitate may be treated with hydrofluoric acid followed by sulphuric acid and ignited again, the loss in weight representing SiO_2 containing 46·93 per cent. Si, or the precipitate may be fused with potassium bisulphate, as described later.

High Silicon Alloys. Ferro-silicon. Samples of ferro-silicon vary a good deal in the ease with which they can be attacked by reagents. If very finely ground, most samples are completely decomposed by aqua regia and may be examined by the following method.

Half a gram of the exceedingly finely powdered alloy is weighed into a 400 c.c. beaker and digested for as long as may be necessary with 10 c.c. of nitric acid and 30 c.c. of hydrochloric acid. When no black specks

can be detected in the residue the cover is removed ar
the bulk of the acids expelled by evaporation; but tl
solution must not go to dryness or the silica will l
contaminated with iron compounds which are almo
impossible to remove. Dilute with about 100 c.c. (
hot water and filter. Wash the precipitate alternatel
with dilute hydrochloric acid and water twice, evapo
rate filtrate and washings to dryness and bake gentl
Take up with sufficient concentrated hydrochlori
acid, dilute, and filter through the same filter pape
Wash completely free from iron, dry the precipi
tate by placing the filter paper point downwards in th
crucible on the hot plate, then ignite very strongl
for at least fifteen minutes, and weigh. If skilfull
carried out this method should yield a perfectly whit
precipitate.

Other Alloys. Where the preceding aqua regia proces
does not give satisfactory results a fusion method ma
be resorted to. Fusion of the finely ground alloy witl
potassium bisulphate may sometimes be used, and
this method has the advantage in speed; but sodium
carbonate intimately mixed with from 10 to 20 pe
cent. of potassium nitrate is effective in every case.
In the potassium bisulphate fusion 0.5 grm. of the alloy
is cautiously heated with 2 grm. of bisulphate in a
porcelain crucible. When fumes escape the crucible
is removed from the muffle and about 15 grm. more
bisulphate are added in two lots, the whole being
finally fused for at least a quarter of an hour at a very
low red heat. The crucible is then removed, cooled,
and boiled out with 20 per cent. sulphuric acid, and

the silica filtered off, washed, ignited, and weighed. A careful examination for unattacked particles should be made. If fusion with alkalies is employed, fuse 0.5 grm. with 10 grm. of the fusion mixture for about half an hour. Cool, dissolve the melt in water, acidify with sulphuric acid (1 : 3), and add about 20 c.c. of concentrated acid in excess. Evaporate to fumes, cool, dilute, filter off, and weigh the silica.

Tungsten and Molybdenum. If these elements are present the alloy must be decomposed with aqua regia. The precipitate is invariably contaminated with tungstic or molybdic oxide. There are several satisfactory but troublesome ways of separating the tungstic oxide, of which may be mentioned heating to just below redness in a stream of air and chloroform vapour; and reducing the two in hydrogen and then passing a current of chlorine at a low red heat. In both these methods the tungsten is carried away as volatile chlorides of varying compositions, while the silica remains and may be weighed. Silica and tungstic acid cannot be satisfactorily separated by means of ammonia, as silica is appreciably dissolved by this reagent. The simplest procedure is to weigh the two together, in a platinum crucible, and then to remove the silica by adding hydrofluoric acid, followed by sulphuric acid. After driving off the excess of acids and igniting the residue, tungstic acid is weighed and silica determined difference.

Other Elements. The ignited precipitate is occasionally found to be contaminated with other elements not generally supposed to cause trouble. In such cases,

where the impurity is of doubtful composition, but probably consists of metallic oxides or basic salts, fusion with potassium bisulphate or pyrosulphate will usually remove the contamination. After dissolving out the melt with water the silica may be filtered off and weighed.

SULPHUR

Sulphur, which is one of the most injurious elements occurring in steel, is present in larger or smaller amounts in all varieties, and its estimation is correspondingly important. The estimation depends on its conversion into either sulphuretted hydrogen or barium sulphate, the former process being generally known as the evolution, the latter as the gravimetric, method. Innumerable modifications and combinations of the two processes have appeared and continue to appear, especially in the German journals. The explanation is to be found in the importance of the estimation and in the great effect which certain details, not usually considered important in other estimations, produce in the results obtained. Without attempting to summarize the literature, the following processes may be relied on to give good results if due attention is given to the points emphasized.

By Evolution. Five grams of the sample in the form of moderately thin drillings or turnings are weighed into a 500 c.c. round flask (Fig. 10). The drillings must not be too thick—about 0·5 mm. ($\frac{1}{50}$ in.) is a desirable thickness. The rubber stopper, carrying a thistle funnel and delivery tube as shown, is placed in position and 50 c.c. of ammoniacal cadmium acetate solution (*see* Appendix I) placed in the 300 c.c. beaker and diluted

with its own volume of water. Hydrochloric acid (50 c.c.) is diluted with 50 c.c. of water and the mixture raised to the boiling-point. The hot hydrochloric acid is now poured down the thistle funnel and the contents

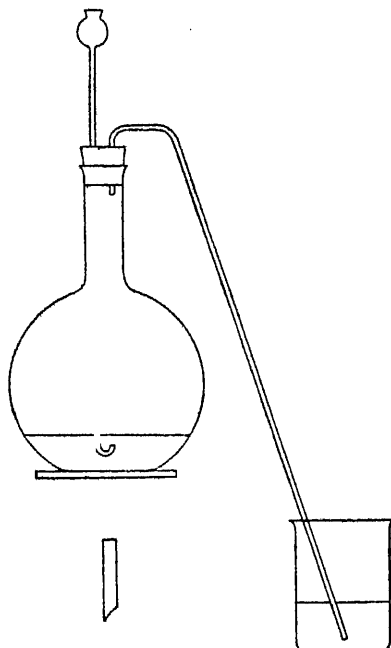
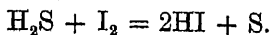



Fig. 10.

of the flask maintained at the boiling-point, but not boiled vigorously, until the steel is completely dissolved. During the solution of the steel, fumes of ammonium chloride rise above the surface of the liquid in the beaker. Experience shows that the absorption by this means is complete, and that a guard absorption tub

is unnecessary. When solution is complete the liquid is boiled for a minute and the flame removed. The most important point in the whole procedure is to make the evolution as rapid as possible. The beaker is then removed and the delivery tube washed into it. The estimation of the precipitated cadmium sulphide may be carried out in various ways, but the following is the simplest method ensuring accuracy. The solution is filtered through a 11 cm. filter paper and washed once with dilute ammonia (10 per cent.). It is unnecessary to wash the precipitate completely free from the mother liquor. The filter paper and precipitate are then placed in a 300 c.c. conical flask and shaken up with about 50 c.c. of water. Sufficient dilute hydrochloric acid is now added just to acidify the liquid, and a small measured excess of standard iodine solution run in. After thoroughly shaking up for about half a minute the excess of iodine is titrated back with standard thiosulphate, using starch solution as indicator. Only the clear starch solution should be added, and if the solution is made up following the directions in Appendix I no difficulty will be experienced in getting the starch solution to settle clear. From the number of c.c. of iodine consumed by the precipitate the percentage of sulphur is calculated from the relation

$$H_2S + I_2 = 2HI + S.$$

Whence 1 c.c. $\frac{N}{10}$ iodine = ·001603 grm. S,

or 1 c.c. $\frac{N}{10}$ iodine = ·03207 per cent. S on 5 grm.

If to 100 c.c. $\frac{N}{10}$ iodine solution are added 60·3 c.c.

of water a solution is obtained containing 7·94 grm. iodine per litre and of which 1 c.c. = ·001 grm. S.

If the filtration of the cadmium sulphide precipitate is omitted and the whole solution titrated as above after just acidifying with hydrochloric acid, practically the same figure is obtained as a rule, but occasionally this leads to high results, owing to the liquid containing some product of the evolution capable of combining with iodine, other than sulphuretted hydrogen.

Gravimetric Estimation. The gravimetric estimation of sulphur in steel, although appearing on the surface perfectly straightforward and simple, is the estimation which gives most trouble to the inexperienced chemist. In view of the frequency with which the estimation has to be made and the conclusions based on the results, the details of the procedure are given here with the greatest fullness, with the reasons for their inclusion.

Five grams of the sample are dissolved in 25 c.c. of hydrochloric acid together with 35 c.c. of nitric acid in an 800 c.c. long beaker. The solution takes place very energetically, and unless a beaker at least of the size mentioned is used, covered with a clock-glass, considerable loss is likely to take place. When the reaction is over the cover is removed, drained into the beaker, and roughly 1 grm. of pure potassium nitrate added. The above proportions of acid are so adjusted that on evaporation a residue of ferric nitrate, not chloride, is left. The solution is now gently evaporated on the hot plate to complete dryness and baked on the hottest part of the plate for half an hour. This baking breaks up the ferric nitrate into ferric oxide and oxides of nitrogen, and at the same time oxidizes away

the soluble carbon compounds and renders the silica insoluble. The potassium nitrate is added with the object of preventing loss of sulphur by the breakdown of ferric sulphate into ferric oxide and sulphur trioxide, the sulphuric acid being assumed to combine with the potassium. Whether this is indeed the case may be considered doubtful, and for low sulphur steels the author has not observed any loss from the omission of this detail; but its retention is desirable, as it is so little trouble to include. The baked mass is now removed from the plate and allowed to cool. The cover is replaced, 40 c.c. strong hydrochloric acid added, and the beaker replaced on the plate and maintained just at the boiling-point until all the ferric oxide has dissolved from the bottom and sides of the beaker. The cover is then removed and drained, and the contents evaporated gently until the volume is reduced to such an extent that a skin begins to form on the surface of the liquid, when 10 c.c. of 5 per cent. hydrochloric acid are added and the beaker removed. During this procedure the last of the nitric acid is removed and the large excess of hydrochloric acid evaporated. This is necessary as barium sulphate does not precipitate well from strongly acid solutions, while nitrates tend to be carried down with the precipitate. The solution is now diluted to about 50 c.c. and filtered through an 11 cm. ashless filter paper into a 200 c.c. beaker. The paper is washed two or three times with water and once with 1 per cent. hydrochloric acid, making the filtrate up to about 100 c.c. The washing of the precipitate can then, if desired, be continued to complete freedom from iron, neglecting the washings, and the

silica ignited and weighed. The filtrate is now boiled with the cover on and, when boiling, 20 c.c. of 10 per cent. barium chloride are run in in a succession of drops from a pipette introduced through the lip of the beaker. The boiling should not be stopped by the addition. If care is exercised no iron salts will dry on the sides of the beaker, but if this has happened they must be re-dissolved after adding the barium chloride by cautiously treating them with a few drops of strong hydrochloric acid from a pipette. The solution is now boiled for a few minutes and allowed to stand for several hours. By adding the barium chloride in the way described above, the barium sulphate is precipitated granular and in a condition to be easily filtered, and precipitation is complete in three or four hours, though it is generally convenient to let the solution stand overnight. The barium sulphate is filtered either through a pulp filter or a close-grained ashless paper. Max Dreverhoff's quantitative barium sulphate filter papers are excellent. It is then washed several times with water and not more than twice with very dilute (1–5 per cent.) hydrochloric acid, using about 5 c.c. each time and washing with water in between. When completely free from chloride two or three more washings are given and the precipitate and paper ignited in an open dish or capacious crucible for about half an hour at a moderate red heat in a muffle. Under these conditions the barium sulphide formed by reduction of the sulphate by the filter ash will be re-oxidized by the air. The dish is then cooled in a desiccator and the contents brushed out and weighed. Treatment of the drecipitate with nitric aud sulphuric acids does not

lead to an increase in weight of more than 1 milligram on a precipitate weighing 2 centigrams.

Determination of Blank. As the reagents employed in this estimation invariably contain small amounts of sulphur, a blank determination is necessary. The conditions of the estimation must be copied as nearly as possible, and this is most conveniently managed either by taking in one case double the quantity of reagents for the same amount of steel, when the difference in the weights of barium sulphate found represents the blank due to the ordinary amount of reagents; or by taking in one case double the amount of steel used in the other case, when the difference between twice the weight of the barium sulphate from the smaller weight of steel and that from the other weight represents the blank. The determination of blank by simply evaporating the reagents with a little potassium nitrate, taking up in hydrochloric acid and precipitating, is unsatisfactory and will lead to errors.

Estimation of Sulphur in Special Steels. When the elements mentioned below are present a modified procedure is necessary.

Vanadium. For low percentages of vanadium either of the above methods may be used, but should the vanadium steel be difficult of solution the evolution method will give low results. With high percentages of vanadium, if silicon is low, the gravimetric method may still be employed, but with silicious ferro-vanadiums a fusion method must be employed. One gram of the alloy powdered as finely as possible is fused with 20 grm. of pure anhydrous sodium carbonate and about 5 grm. of potassium nitrate for half

an hour. The melt is dissolved out with water aci
with hydrochloric acid and evaporated to dry
The mass is taken up with dilute hydrochloric
filtered, again evaporated to dryness, and take
again with as little dilute hydrochloric acid as pos
It is now filtered if necessary, diluted to about 10(
and precipitated with barium chloride as above.

Silicon. High silicon steels and ferro-silicon
usually be dissolved by aqua regia, but after evapo
to low bulk the solution should be diluted an
bulk of the silica separated before evaporati
complete dryness and baking; otherwise the silic
take up a considerable amount of other matter.
this alteration the gravimetric method may be emp
but in view of the difficulty of solution the evo
method is inapplicable.

Titanium. Titanium steels present no addi
difficulties. With ferro-titanium the evolution m
may generally be used, but a fusion method is
satisfactory. Proceed as in ferro-vanadium, but e
the melt with water only, whereby all the consti
except aluminium, phosphorus, silicon, vana
tungsten, and molybdenum (if present) remain
residue. A second fusion may be necessary.
united filtrates are then acidified with hydroc
acid, evaporated to dryness, taken up in hydroc
acid, filtered, diluted to about 100 c.c., and precip
with barium chloride.

Tungsten and Molybdenum. The evolution m
is not applicable as tungsten alloys are not com
decomposed in all cases, while both elements p
the complete evolution by forming an insoluble sul

The gravimetric method is usually applicable without alteration in the presence of molybdenum, but tungstic acid is precipitated in varying amounts with the barium sulphate, if not completely eliminated along with the silica. The precipitate may be freed from these impurities by filtering on pulp and boiling the washed precipitate and pulp with 30 per cent. ammonia, afterwards re-collecting the precipitate and pulp and washing with ammonia. If aqua regia will not completely dissolve the alloy it should be fused with four or five times its weight of potassium nitrate, cooled, boiled out with water, the dish removed. Hydrochloric acid is added, and the solution evaporated to dryness, again taken up with hydrochloric acid, filtered, and the estimation continued as in steel; but the same precautions should be taken as before to avoid contamination of the precipitate with tungstic or molybdic acid.

TITANIUM

TITANIUM is a fairly common constituent of stee especially American varieties, but the amount doe not often exceed 1 per cent. Its office is similar t that of vanadium—to eliminate impurities by carryin them into the slag—and it has been credited with very beneficial effect in removing nitrogen. If speciall added to steel, a rich ferro-titanium alloy is mad use of, which may contain up to 80 per cent. o titanium.

In steel, the most convenient mode of estimation i to make use of the colour developed with hydroge peroxide by titanic compounds dissolved in nitric o sulphuric acids, but a gravimetric method dependin on the precipitation of titanic acid and ignition of thi compound to oxide may be used. Ferro-titanium vary a good deal in their behaviour—chiefly in th readiness with which they pass into solution—an the titanium content is most conveniently estimate volumetrically together with the iron, and the latte estimated separately and allowed for.

Colorimetric Estimation. This method is only appli cable in the absence of vanadium. Dissolve 1 grm of the steel under examination and 1 grm. of a simila steel containing no titanium separately in 20 c.c. o 1 : 3 sulphuric acid, boiling thoroughly. If any con

siderable amount of carbon remains, it should be filtered off and examined qualitatively for titanium, but this is not usually necessary. Cool, and dilute to about 50 c.c. in comparison cylinders. Add to both 10 c.c. of hydrogen peroxide solution (*see* Appendix I), and stand for a few minutes. Match the colour produced in the sample by adding to the other a sufficient amount of the standard titanium solution (*see* Appendix I), and hence calculate the percentage. The estimation may also be performed on the same sample as that for manganese by the bismuthate method, if the permanganate colour is just cleared up, by adding a drop of ferrous sulphate, and this saves the trouble of weighing another sample.

Care should be taken that the comparison solution is in all respects similar to the other, especially in respect of nickel, copper, molybdenum, and chromium content. Molybdenum and chromium, if present in fair amount, make the estimation unreliable.

Gravimetric Method. Dissolve the sample (5 grm.) in 50 c.c. 1 : 3 sulphuric acid with the aid of heat. If the residue is very small the estimation may be continued; but if it is considerable it should be filtered off, ignited, fused with sodium carbonate, and the mass returned to the solution. Evaporate the whole until fumes begin to appear. Dilute carefully and filter off the silica. Add a small excess of sulphur dioxide, heat to near boiling, and add ammonia until a small permanent precipitate forms. Clear this up with a drop or two of sulphuric acid—avoiding excess. Add 10 grm. of sodium thiosulphate, boil thoroughly, and allow to settle. Filter, and wash the precipitate with

very dilute warm acetic acid. Ignite, and weigh as TiO_2 containing 60·0 per cent. Ti.

If the estimation is carried out as above, the precipitate should be free from everything but traces of iron, aluminium, and phosphorus. Iron may be completely eliminated by re-solution in sulphuric acid and re-precipitation; but aluminium and phosphorus, if present in any quantity, must be eliminated by fusion with sodium carbonate and extraction with water.

Ferro-Titanium. Either the gravimetric method just described may be used—working on 0·5 grm. instead of 5 grm.—or the following volumetric method. Ferro-titaniums generally dissolve pretty readily in moderately dilute acids, but in some cases fusion with potassium bisulphate may be resorted to with advantage. If potassium bisulphate is used, it is well first to fuse it alone, and to add the weighed sample when the surface has solidified. Fifteen minutes fusion at not too high a temperature is usually ample—and it should not be possible to detect any gritty particles after that time on stirring with a platinum wire. The crucible and contents are then cooled, and boiled with dilute sulphuric acid. If the gravimetric method is employed the whole is evaporated to fumes to separate silica and the estimation continued as above.

With some varieties of ferro-titanium containing high silicon, fusion with bisulphate is insufficient. In these cases the alloy may be first roasted in a platinum crucible, cooled, treated with hydrofluoric acid, evaporated, and then fused with bisulphate; or it may be roasted, fused with sodium carbonate and potassium nitrate, and dissolved from the crucible with nitric or sulphuric acid.

Volumetric Estimation. Dissolve 1 grm. of the alloy in dilute sulphuric acid (25 c.c. 1 : 3). If the alloy does not dissolve readily, solution must be effected by one of the methods indicated above. If any considerable residue remains after the action of the acid has stopped it must be filtered off, fused with sodium carbonate and a little sodium peroxide, dissolved out in sulphuric acid, evaporated to fumes, diluted, filtered from silica, and the filtrate added to the main solution. The solution is now diluted to exactly 250 c.c. in a measuring flask, and two quantities of 100 c.c. each (= 0·4 grm. sample) withdrawn. To one portion is added about 50 c.c. of sulphurous acid solution, and the liquid is then boiled vigorously in a flask covered with a watch-glass until all sulphur dioxide has been expelled. The solution is then cooled and titrated with standard permanganate—the titration representing the iron present. While these operations are being carried out the other 100 c.c. portion is treated with about 2 grm. of pure zinc foil (free from iron) in a covered flask and left to simmer gently on the hot plate, a little more acid being added if necessary. Small amounts of titanium (under 0·1 grm.) are quickly reduced, but for safety it is well to let the reduction occupy at least fifteen minutes. When all the zinc has been dissolved, 5 grm. of iron alum, dissolved in 25 c.c. of well-boiled water, is added, and the solution quickly cooled and titrated with permanganate. The difference between this titration and the preceding one represents the amount of permanganate reduced by the titanium—1 c.c. $\frac{N}{10} KMnO_4 = \cdot 00481$ grm. Ti.

TUNGSTEN

TUNGSTEN is one of the commonest additions to moder
steels. It confers the property of retaining magneti
zation over long periods and, with other metals, is
constituent of most of the self-hardening and high
speed steels so widely used at the present day.
fairly large selection of methods for its estimation i
available, most of which terminate with the weighin
of the tungsten as tungstic oxide, though lead tungstat
is an alternative form. Volumetric methods for it
estimation have not so far been employed, though
doubtless a method could be readily devised dependin
on the solution of tungstic acid in standard alkali and
titration of the excess.

Rapid Estimation. The following method is rapid
and widely used. It is stated to yield slightly low
results, but the author has not found this to be the
case. Dissolve 5 grm. of the sample as far as possible
in 80 c.c. strong hydrochloric acid, and when action
slackens add cautiously just enough strong nitric acid
to oxidize the iron and effect solution. Remove the
cover and evaporate until tungstic oxide begins to
separate, add 80 c.c. of hot water, and boil. The
precipitated tungstic acid is allowed to settle in a
warm place, filtered off, and washed alternately with
hot water and very dilute hydrochloric acid. The

precipitate contains generally as impurity ferric oxide, silica, and possibly chromium and titanium oxides in traces. If the amount of these is not negligible, the silica should be removed by means of hydrofluoric and sulphuric acids. The tungstic acid is then extracted from the residue by warming with a little dilute ammonia, the insoluble matter filtered off, and the filtrate evaporated to dryness in a platinum dish and ignited. The weight of WO_3 obtained, multiplied by 0·7931, represents tungsten. Another equally satisfactory method is to fuse the precipitate of impure tungstic oxide with potassium bisulphate, raising the temperature gradually to a red heat, when the fusion should be clear and transparent. The fusion is boiled out with ammonium carbonate solution, the insoluble matter collected, ignited, and weighed. This weight when subtracted from the weight of the original precipitate gives the weight of the tungstic oxide present.

The above method may be used for the estimation of tungsten in all high-speed steels, and is not interfered with, except as mentioned above, by *chromium*, *molybdenum*, *nickel*, *cobalt*, or *vanadium*.

URANIUM

URANIUM is a somewhat rare addition to steel, and when present is always the result of an intentional addition. It is stated to confer properties on the metal similar to those due to nickel, *i.e.* toughness and resistance to shock, but to a more marked extent. The following method is largely based on Brearley's monograph "The Chemistry of Uranium," and has been found to work well.

Estimation. Dissolve 10 grm. of steel in 50 c.c. strong hydrochloric acid diluted with 50 c.c. hot water. If more than ·1 per cent. of silicon is present it must be eliminated by taking to dryness, baking, and re-dissolving in hydrochloric acid (40 c.c.). Copper, if present, is eliminated by diluting to about 300 c.c. and passing sulphuretted hydrogen. The precipitated copper sulphide is filtered off together with the silica, and the solution boiled to eliminate sulphuretted hydrogen. About ten times as much microcosmic salt as there is uranium present is now added, followed by ammonia till a faint permanent precipitate is produced. This is cleared up with the smallest possible excess of hydrochloric acid, and 10 grm. of sodium thiosulphate and 15 c.c. of acetic acid are added and the solution boiled for about fifteen minutes. It is then allowed to settle and the precipitate filtered off. The mixed phosphates

of aluminium, iron, and uranium are then dissolved in a little nitric acid (1·2) and the solution rendered only feebly acid by ammonia. It is then heated nearly to boiling and poured into about 100 c.c. warm 10 per cent. ammonium carbonate solution, which is vigorously stirred the while. The solution is now preferably set aside in a warm place for an hour or two, and then filtered. The solution, containing the uranium, is brought to boiling, microcosmic salt ten times the weight of the uranium added, and nitric acid till just neutral. Ten grams of sodium thiosulphate and 15 c.c. acetic acid are added, and the solution boiled fifteen minutes as before. The precipitate is filtered off, washed, and ignited. The green residue, which is rather hygroscopic, is weighed and contains 68·55 per cent. uranium. As this figure does not correspond to a simple chemical compound, it is preferable to convert it into uranyl pyrophosphate $(UO_2)_2P_2O_7$ by treating with a very little nitric acid and igniting at low redness. The yellow mass of uranyl phosphate obtained contains 66·81 per cent. U. It is also rather hygroscopic, and should be kept in a good desiccator and weighed without delay.

VANADIUM

VANADIUM is seldom or never added to steel in considerable quantity with the intention of preparing an alloy steel of superior qualities. It is chiefly used as a "scavenger" to eliminate impurities by combining with them and carrying them into the slag. As a result vanadium steel usually contains well under 1 per cent. of vanadium; but ferro-vanadium alloys, which are made use of as a convenient vehicle for adding the vanadium, may contain 30 or 40 per cent.

The detection of vanadium offers no great difficulties as its reactions are at once delicate and characteristic. Usually it is sufficient to dissolve about ·2 grm. of the sample in dilute sulphuric acid (1 : 3), adding a slight excess of nitric acid to oxidize the iron and complete solution, followed by a few drops of hydrogen peroxide to the cold diluted liquid. A dark brownish-red coloration indicates vanadium. The colour is almost discharged by adding a fair excess of ferrous sulphate. Titanium under the same conditions yields a bright straw-yellow solution, but the vanadium colour is always clearly distinguishable even when considerable amounts of titanium are present. The titanium colour is not at all readily discharged by a considerable excess of ferrous sulphate. Another very characteristic reaction is the rapid formation of a black colour on heating

a little of a vanadium solution with a solution of aniline in dilute sulphuric acid, which also contains a little potassium chlorate. The colour is at first purple, then deep plum, and finally black, and is due to the production of aniline black, resulting from the accelerated oxidation of the aniline by the chlorate in presence of vanadium compounds. The most sensitive test is Gregory's (*C.N.*, 1909, 100, 221), which is not interfered with by titanium, molybdenum, or tungsten, even if present in large quantities, but iron and chromium must be separated. The solution, containing a little potassium chlorate, is taken to fumes with sulphuric acid until all chlorine is evolved and cooled. Twenty cubic centimetres of a solution of strychnine in concentrated sulphuric acid (4 grm. per litre) are then added. An intense colour immediately develops if vanadium is present, and attains its maximum intensity in about ten minutes. By comparison with a similarly treated standard a colorimetric estimation may be made.

Separation from Iron and other Constituents of Steel. By pouring a nearly neutralized solution of the steel into boiling 10 per cent. caustic soda, vanadium is completely separated as soluble vanadate from iron, nickel, manganese, copper, and all but traces of chromium; but molybdenum, tungsten, titanium, and aluminium remain associated. The addition of ammonia containing about 5 per cent. ammonium phosphate (Am_2HPO_4) to a solution of the steel precipitates iron, manganese, aluminium, and chromium and leaves the vanadium in solution with copper, and part of the nickel, tungsten, and molybdenum. After dissolving the steel in aqua regia and evaporating to dryness and

fusing the mass with sodium carbonate, adding about 0·5 grm. of finely powdered charcoal during the last ten minutes of the fusion, and then cooling and extracting with water, vanadium is separated from chromium, and passes into solution with the tungsten, molybdenum, and aluminium. Vanadium may be separated from all metals except molybdenum by proceeding as in the ordinary phosphorus determination, but adding about ten times its weight of sodium phosphate before adding the molybdate. The vanadium is then all included in the phospho-vanadio-molybdate precipitated.

Estimation. In view of the difficulty of effecting a satisfactory separation, vanadium is not conveniently estimated gravimetrically in complex steels. Volumetric methods, many and various, have been described, and though most approximate to the vanadium content, few accurate methods are known. Quinquevalent vanadium is reduced to the quadrivalent condition in acid solutions by sulphurous acid, ferrous sulphate, oxalic acid, and some other reagents, and is re-oxidized by permanganate readily at 60–70° C., and slowly at lower temperatures. Bichromate does not effect reoxidation, but quadrivalent vanadium reduces to some extent the ferric salts of the mineral acids, producing ferrous iron; so that when the quinquevalent compound is reduced by an excess of ferrous sulphate, bichromate cannot be used to estimate the excess of ferrous sulphate added unless special precautions are taken. If, however, sodium phosphate considerably more than equivalent to all the iron present be added, this reduction may be avoided and bichromate used. Without going into an exhaustive criticism of published

methods, the following procedures will be found reliable.

Colorimetric Estimation. Dissolve 1 grm. of the sample and 1 grm. of a similar steel free from vanadium in 10 c.c. of 1 : 3 sulphuric acid. To each add cautiously 2 c.c. strong nitric acid, heat till the solutions are clear and fumes have disappeared, and cool. Transfer to comparison glasses, and to each add 10 c.c. of hydrogen peroxide solution made by dissolving about 2 grm. of sodium peroxide in 100 c.c. sulphuric acid (1 : 10). Dilute with water until the solutions are equal in volume, and match the colour produced by the vanadium steel by adding to the other a sufficient quantity of a standard solution of vanadium containing 0·1778 grm. V_2O_5 dissolved in 10 c.c. strong sulphuric acid and diluted to 1 litre (1 c.c. = ·0001 grm. V).

The above procedure can hardly yield results accurate to 0·04 per cent., but the following method is much more sensitive. Dissolve 1 grm. of the sample in 45 c.c. nitric acid (1 : 2) and add 1 c.c. 10 per cent. sodium phosphate. Boil till all fumes are off. Cool somewhat and add carefully 14 c.c. of ammonia (1 : 1), boil until all ferric hydrate is re-dissolved, remove from the plate, and add 30 c.c. of nitro-molybdate solution, shaking well. The vanadium is all co-precipitated with the phospho-molybdate. Filter off on a small smooth filter and wash free from iron with 2 per cent. nitric acid, finally washing with water. Wash the precipitate into a 400 c.c. beaker, add a small pinch of potassium chlorate and, cautiously, 20 c.c. of strong sulphuric acid, and evaporate on the hot plate till fumes are freely evolved. Remove and cool. Take an amount

of the standard vanadium solution roughly equivalent to the expected amount of vanadium present, add a little potassium chlorate and, cautiously, 20 c.c. of sulphuric acid, take to fumes and cool as before. When cold add to each 20 c.c. of a solution of 4 grm. of strychnine in 1 litre of strong sulphuric acid. Allow to stand ten minutes and match the colours by diluting the stronger with sulphuric acid.

Gravimetric Estimation. The following modification of Blair's method, though rather long, gives good results: Dissolve 5 grm. of a steel or pig-iron and correspondingly less of a high vanadium alloy in 50 c.c. of 1·2 nitric acid. Evaporate to dryness and bake until nitrates are decomposed, taking care that the mass does not splash up on to the sides of the beaker. The mass can then be easily removed from the beaker with a negligible loss. Powder in an agate mortar and fuse with 25 grm. of sodium carbonate and 2 grm. of sodium peroxide in a platinum dish for half an hour at a bright red heat. Boil out the fused mass with water, filter, and nearly neutralize with nitric acid (1·2). Boil off the carbon dioxide, filter if necessary, dilute to 500 c.c. and just acidify—a yellow colour showing the presence of vanadium. Add 5 grm. of mercurous nitrate dissolved in as little water as possible and a small quantity of mercuric oxide suspended in water to neutralize the free acid. Boil, filter, and wash with hot water, and ignite carefully after drying. If chromium, tungsten, and molybdenum are absent, the residue will consist of vanadium pentoxide, and the weight of vanadium present may be calculated by multiplying by 0·5655. If present, the precipitate

must be again fused with 10 grm. of sodium carbonate and 1 grm. sodium peroxide as before, dissolved in a little water and filtered if necessary. Pure ammonium chloride is then added to saturation—about 3·5 grm. will be needed for each 10 c.c.—the solution is well stirred and allowed to stand for some time. The vanadium is precipitated as ammonium metavanadate, and may be filtered off, washed with saturated ammonium chloride containing ammonia, ignited, and weighed as pentoxide.

Volumetric Estimation. The volumetric estimation of vanadium by the following method is much more rapid than the gravimetric and quite as accurate if performed with care. Dissolve 0·5 grm. of ferro-vanadium, or 2·5 grm. of a vanadium steel, in 30 c.c. of sulphuric acid (1 : 3), adding 10 c.c. of nitric acid as the reaction slackens. A little hydrofluoric acid will effect solution if the sample is refractory. Evaporate until fumes are freely evolved. Dilute with 100 c.c. 1 : 3 sulphuric acid and then with water to 400–500 c.c. Heat to about 60° or 70° and add dilute permanganate solution drop by drop until a faint pink colour persists. Discharge this colour by carefully adding the exact amount of ferrous sulphate necessary. Now add 50 c.c. of 10 per cent. sodium phosphate solution and cool. Add an excess of standard ferrous sulphate solution and titrate back with bichromate, using ferricyanide of potassium as an external indicator. The amount of ferrous sulphate added, less that equivalent to the bichromate used in the back titration, represents the amount oxidized by the vanadium. 1 c.c. $\frac{N}{10}$ ferrous

sulphate = ·00510 grm. V. This method is interfered with by chromium, but not by any other metal commonly occurring in steel. The effect of chromium may be avoided by performing the first oxidation with permanganate in the cold solution instead of at 65°, but care must be taken that enough permanganate is added to produce a really permanent coloration.

NOTE ON THE ESTIMATION OF PHOSPHORUS IN STEELS CONTAINING ARSENIC

In view of the contradictory statements as to the co-precipitation of arsenic with ammonium phospho-molybdate, the following results obtained by the methods described in the foregoing pages are of some interest.

The steel employed was supplied to the author with the following analysis :

C	0·435
Mn	0·835
Si	0·10
P	0·040
As	Present but not estimated.

Phosphorus was first estimated by the quick method (p. 68) and the mechanicalized method without separation of arsenic (p. 72). Three estimations by each method were made—in the first no more arsenic was added, but in the second and third, roughly, 0·05 and 0·10 per cent. of arsenic respectively was weighed out as As_2O_3 and added to the drillings before dissolving.

The results are shown below.

	I	II	III
	PER CENT.	PER CENT.	PER CENT.
Arsenic added . .	Nil	0·05	0·10
P found — Quick method .	0·041	0·039	0·040
P found — Mechanicalized method .	0·065	0·103	0·127

Other estimations were carried out by the mechanicalized "arsenic separated" method (p. 73) and the long method (p. 70), and these gave:

	I	II
	PER CENT.	PER CENT.
Mechanicalized, arsenic separated .	0·039	0·038
Long method	0·040	

It is evident from these figures that arsenic only affects the short mechanicalized method, which is designed to carry down the whole of the arsenic with the phosphorus, and is on that account useful as showing the combined As + P figure, and admits of the simple estimation of arsenic by difference. It is, of course, impossible to disprove the statement that in some steels the arsenic present behaves differently from added arsenic. It is also possible that in certain cases higher silicon or other impurities may vitiate the quick method, although no difficulty has been encountered so far from these causes.

ATOMIC WEIGHTS

		O=16
Aluminium	Al	27·1
Antimony	Sb	120·2
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Copper	Cu	63·57
Fluorine	F	19·0
Glucinum	Gl	9·1
Gold	Au	197·2
Hydrogen	H	1·008
Iodine	I	126·92
Iron	Fe	55·84
Lead	Pb	207·10
Lithium	Li	6·94
Magnesium	Mg	24·32

		O=1
Manganese	Mn	54·9
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Nickel	Ni	58·6
Nitrogen	N	14·0
Oxygen	O	16·0
Palladium	Pd	106·7
Phosphorus	P	31·0
Platinum	Pt	195·2
Potassium	K	39·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·8
Sodium	Na	23·0
Strontium	Sr	87·6
Sulphur	S	32·0
Tantalum	Ta	181·5
Tellurium	Te	127·5
Thorium	Th	232·4
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·0
Zinc	Zn	65·3
Zirconium	Zr	90·6

APPENDICES

APPENDIX I

SOLUTIONS

Acetate of Ammonia:

Ammonia (·880)	100 c.c.
Glacial acetic acid . . .	114 c.c.
Water	228 c.c.

Mix the ammonia with the water and add the acetic acid. Solution should just redden blue litmus.

Acetate of Cadmium for estimation of sulphur by evolution method:

Crystallized cadmium acetate .	25 grm.
Ammonia (·880)	100 c.c.
Water up to	1000 c.c.

Dissolve the cadmium acetate in part of the water, add the ammonia, and dilute to 1000 c.c. Filter if necessary.

Bichromate of Potassium, standard, for chromium:

Pure crystallized $K_2Cr_2O_7$ . .	2·830 grm.
Dissolve in water and dilute to .	1000 c.c.

1 c.c. = ·001 grm. Cr.
= ·003159 Fe.

Bichromate of Potassium—(*cont.*).

$$1 \text{ c.c.} = \cdot 004513 \ Fe_2O_3.$$
$$= \cdot 5770 \text{ c.c.} \frac{N}{10} KMnO_4.$$
$$= \cdot 0006334 \text{ grm. Mn as } KMnO_4.$$
$$= \cdot 001583 \text{ grm. Mn as } MnO_2.$$
$$= \cdot 007320 \text{ grm. I.}$$

Carbonate of Sodium, for standardizing acid for] phorus determination:

Pure anhydrous sodium carbonate	3·915 grm
Water up to	1000 c.c.

The standard sulphuric acid should be almost ex equivalent. The number of cubic centimetres of equal to 1 c.c. of the above solution = ·0001 grm. I

Carbonate of Sodium, decinormal:

Pure anhydrous Na_2CO_3 . . .	5·303 grm.
Water up to	1000 c.c.

Chloride of Calcium, for arsenic estimation.

Anhydrous calcium chloride . .	400 gm.
Hydrochloric acid	400 c.c.
Water to	1000 c.c.

Add the calcium chloride to a small quantity of wa then add the acid and dilute to 1000 c.c.

Cyanide of Potassium for nickel estimation :

Cyanide of potassium, crystallized	10 grm.
Stick potash, about . . .	10 grm.
Water	2500 c.c.

Dissolve in a small quantity of water and place in a Winchester, adding water until nearly filled. Shake well. This solution is roughly equivalent to the silver nitrate solution used in nickel estimation.

Copper Standard:

Re-crystallized $CuSO_45H_2O$ . .	39·30 grm.
Water up to	1000 c.c.

10 c.c. = 0·1 gm. Cu.

Hydrate of Sodium, for phosphorus determination:

Caustic soda, purified by alcohol .	8 grm.
Barium hydrate, crystallized .	1 grm.

Water up to one Winchester.

Dissolve separately in water, mix in a Winchester, add water till nearly filled, shake, and allow to settle. 1 c.c. is roughly equal to 1 c.c. sulphuric acid.

Iodide of Potassium for indicator in cyanometric nickel determination:

Potassium iodide . . .	4 grm.
Water up to	100 c.c.

Iodine, for volumetric estimation of sulphur:

Pure re-sublimed iodine . .	7·96 grm.
Potassium iodide . . .	12·0 grm.
Water to	1000 c.c.

Dissolve the potassium iodide in a little water and add it in small quantities to the iodine, pouring the strong solution into a litre flask before adding more iodide solution. When all the iodine has been dissolved dilute to 1 litre.

1 c.c. = ·001 grm. S.
= ·02 per cent. on 5 grm. samples.
= ·01 per cent. on 10 grm. samples.

Molybdate Solution, for precipitating phosphorus by the quick method:

Pure molybdenum trioxide . .	150 grm.
Ammonia (·880) . . .	105 c.c.
Water	315 c.c.

Mix the ammonia and water, and add to the molybdic oxide. Stir till nothing further goes into solution, and filter. Pour the filtered liquid with constant stirring into

Nitric acid (1·2) . . .	1875 c.c.

Molybdate Solution, for both long and mechanicalized methods:

Ammonium molybdate . .	260 grm.
Water to fill . . .	1 Winchester quart.

Dissolve the ammonium molybdate in warm water and mix in the Winchester.

Nitrate of Silver, for cyanometric nickel estimation:

Pure re-crystallized silver nitrate .	5·792 grm.
Water to	1000 c.c.

1 c.c. = ·001 grm. Ni.
= ·003833 Ag.

Nitric Acid, sp. gr. 1·2:

Concentrated nitric acid (1·42) .	2 volumes.
Water	3 volumes.

Nitric Acid, sp. gr. 1·135:

Concentrated nitric acid (1·42) .	2 volumes.
Water	5 volumes.

Nessler's Solution:

Potassium iodide	62·5 grm.
Mercuric chloride	103 grm.
Stick potash	150 grm.

Dissolve the potassium iodide in about 250 c.c. and the mercuric chloride in 400 c.c. of water, and set apart a few c.c. of each. Add the mercuric chloride until a permanent precipitate is just produced, clear this up by adding the remainder of the potassium iodide, then add more mercuric chloride very carefully until a precipitate is just produced again. Now dissolve the potash in 150 c.c. of water, add it to the solution and dilute to 1 litre.

8

Nitrogen Standard:

Pure re-crystallized ammonium chloride	0·1909 grm.
Ammonia-free water up to . .	1000 c.c.

1 c.c. = ·00005 grm. N.

Permanganate of Potassium, decinormal:

Pure re-crystallized permanganate of potassium	3·16 grm.
Water up to	1000 c.c.

Add the water in small quantities to the permanganate in a flask. Shake round and pour off the concentrated solution into a litre flask and repeat until all is dissolved. Then dilute to 1 litre.

1 c.c. = 0·1 per cent. Mn on 1·1 grm. samples.
= ·001734 grm. Cr as CrO_3.
= ·005584 grm. Fe.

Permanganate of Potassium, for oxidizing phosphorus:

Potassium permanganate . .	30 grm.
Water up to	1000 c.c.

Peroxide of Hydrogen, for titanium and vanadium estimations:

Sodium peroxide . . .	6–7 grm.
Sulphuric acid (1 : 3) . . .	250 c.c.
Water to	1000 c.c.

Dissolve the peroxide in the acid and dilute. The solution is roughly decinormal.

Starch Solution:

Take about a level teaspoonful of starch, and make into a thin paste with a few c.c. of water. Add two or three drops of saturated zinc chloride solution and pour into 400 c.c. of boiling water. Boil for one minute and allow to settle. The cell walls will quickly subside and the clear supernatant liquid may be poured off and used.

Sulphate of Iron and Ammonia, equivalent to standard bichromate:

Pure crystallized ferrous ammonium sulphate	22·6 grm.
Concentrated sulphuric acid .	100 c.c.
Water up to	1000 c.c.

Add the sulphuric acid to about 500 c.c. of water and dissolve in it the ferrous ammonium sulphate. Cool and dilute to 1 litre.

Sulphate of Iron and Ammonia, equivalent to decinormal permanganate:

Pure re-crystallized ferrous ammonium sulphate	39·1 grm.
Concentrated sulphuric acid .	100 c.c.
Water up to	1000 c.c.

Prepare as for preceding solution.

Sulphuric Acid, for phosphorus determination:

Concentrated pure sulphuric acid .	2·02 c.c.
Water up to	1000 c.c.

1 c.c. = ·0001 grm. P.

Sulphuric Acid, decinormal:

Concentrated sulphuric acid .	2·72 c.c.
Water up to	1000 c.c.

This acid must be standardized against $\frac{N}{10}$ sodium carbonate.

Thiosulphate of Sodium, for volumetric sulphur estimation:

Crystallized sodium thiosulphate .	15·50 grm.
Water up to	1000 c.c.

1 c.c. = 1 c.c. iodine = ·001 grm. S.

Titanium Standard:

Pure titanium dioxide . .	0·8340 grm.

Fuse with 8–10 grm. of sodium carbonate. Dissolve in a mixture of 50 c.c. water and 50 c.c. strong sulphuric acid, evaporating until solution is complete. Then dilute to 500 c.c. 1 c.c. = ·001 grm. Ti.

Tartrate of Ammonia, for keeping Al and Fe in solution:

Tartaric acid	340 grm.
Ammonia (·880) . . .	500 c.c.
Water	500 c.c.

Mix the ammonia and water, add to the tartaric acid, and filter if necessary. 30 c.c. of the solution will keep 1 grm. Al in solution.

Vanadium Standard:

Pure vanadium pentoxide . .	0·1778 grm.
Sulphuric acid, conc. . . .	10 c.c.
Water to	1000 c.c.

Dissolve the vanadium pentoxide in the strong acid with the aid of heat if necessary, and dilute to 1 litre when cool.

1 c.c. = ·0001 grm. V.

APPENDIX II

ANALYSES OF DIFFERENT STEELS AND ALLOYS

Although steel is seldom bought and sold on chemical analysis alone, specifications frequently impose limits on the proportions of the various constituents, especially of carbon, silicon, manganese, sulphur, and phosphorus, which may be present.

The following details of the amounts of various elements commonly present in different classes of steel will serve as a guide to what may be expected in good quality British steels, but it may easily happen that steel admirably suited to its purpose may be of a composition not falling within these bounds. The ferro-alloys are typical, but alloy steels of the most varying composition may be encountered.

	C	*Si*	*Mn*	*S*	*P*
Axles					
		Not above		Under	Under
	$0{\cdot}3 \pm 0{\cdot}05$	0·2	0·6–1·0	·045	·045
Fishplates					
		Under		Under	Under
	0·15–0·25	0·06		0·06	0·08

	C	Si	Mn	S	P
Girders					
Acid open hearth	0·15–0·25	0·06	0·80	0·06	0·06
Basic open hearth	Do.	Do.	Do.	Do.	0·04
Hammers					
	0·50–0·75	0·2	0·2	0·02	0·02
Cold Chisels, Knives					
	1·0–1·3	0·2	0·3	·015–·02	·015–·02
Rails					
Acid Bessemer	0·35–0·50	0·06–0·10	0·7–0·95	Under 0·08	Under 0·08
Basic open hearth	0·45–0·65		0·65–0·90	0·06	0·06
Razors					
	1·3–1·5	0·2	0·2	Under 0·020	Under 0·020
Springs					
Laminated	0·45–0·70	Under 0·25	0·5–0·8	Under 0·04	Under 0·035
Spiral	0·8–1·3	Under 0·12	Under 0·8	Under 0·035	Under 0·035
Tyres					
	0·35–0·70	Under 0·35	Under 0·9	Under 0·045	Under 0·045

STEEL-MAKING ALLOYS

Ferro-chrome

	Blast Furnace	Electric Furnace
C	9	0·5–9·0
Si	under 1	all very low
S	·05	
P	·05	
Mn	·4	
Fe	30–45	19–27
Cr	45–60	60–70

Ferro-manganese

	English	Russian
C	5–7	7
Si	0·1–0·7	1·5
S	Trace	Trace
P	0·1–0.25	0·3
Mn	50–90	91

Ferro-molybdenum

C	0·3–6·5
Si	0·05–0·20
Mn	under 0·2
S	0·02–0·05
P	0·01–0·03
Mo	50–85

Ferro-nickel

C	0·5–1·0
Si	0·1–0·3
Mn	under 0·3
S	under 0·04
P	0·02–0·04
Ni	25–75

Ferro-silicon

Low Grade		Electric Furnace	
C	1–2	C	0·1–0·5
Si	8–20	Si	25–90
Mn	1–4	Mn	0·1–0·3
S	0·015–0·05	S	0·01–0·04
P	0·04–0·15	P	0·04–0·20

Ferro-titanium

	Low Grade	High Grade
C	0·5–0·8	0·5–3·0
Si	0·05–0·40	0·7–1·3
Mn	under 0·1	0·2–0·3
S	0·02–0·03	0·02–0·05
P	0·03–0·05	0·02–0·03
Ti	10–12	50–60

Ferro-tungsten

C	0·4–3·3
Si	0·1–1·9
Mn	·05
S	0·01–0·10
P	under 0·05
W	50–85

Al, Ni, and Cr sometimes up to 1 per cent.

Ferro-vanadium

C	1·0–4·0
Si	0·1–0·4
Mn	0·15–0·6
S	0·03
P	0·03
V	35–55

Molybdenum, metallic

C	0·5–5
Si	under 0·5
Mn	under 0·1
S	under 0·05
P	absent
Mo	94
Al	sometimes up to 1 per cent.

Nickel, metallic

C	Trace–0·2
Si	Trace–0·2
Mn and P	Traces
S	Trace–0·05
Cu	0·1
Fe	Trace–0·50
Co	up to 3
Mg and Al	Traces

Spiegeleisen

	English	Silico Spiegel	Silico Manganese	
			I	II
C	5	1–2	0·20–0·25	0·20–0·2
Si	0·4–1·0	10–15	25–30	21–26
Mn	10–25	20–25	65–70	50–55
S	0·01	0·01–·03	Trace	Trace
P	0·05	0·015	·10–·13	·10–·1
Cu, Ni, As			Nil	Nil

Tungsten, metallic

C	0·1–0·3
Si	0·5
Mn	under 0·2
S	Nil
P	Nil
W	97–99
Mg, Al, and O	up to 1 per cent.

ALLOY STEELS

Mushet Self-hardening (Air-hardening) Steel

C	2·15
Si	0·10 to 1·3
Mn	1·5 to 3·0
S	0·010–0·50
P	0·010–0·80
Cr	0–3·5
W	5–10

High-Speed Steels

Typical Analysis	C	0·7
	Si	0·05
	Mn	0·10
	S	0·010
	P	0·010
	V	0·30
	W	18·0
	Cr	5·7

The composition of these steels is very variable and may range within the following limits :

C	0·3–1·3
Si	0·04–1·4
Mn	0·05–0·30
S	0·010–0·060
P	0·010–0·040
V	under 1·0*
W	10–25
Mo	0–8
Cr	1·5–6

* As a rule, but varies within wide limits.

INDEX

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